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# THE CYANIDE INDUSTRY

THEORETICALLY AND PRACTICALLY  
CONSIDERED

BY

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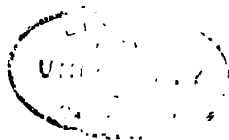
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## TRANSLATOR'S PREFACE.

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THE publication of Robine and Lenglen's "*L'Industrie des Cyanures*" in the series *Encyclopédie Industrielle* in France is a good indication of the value of the work.

The translation of this book into English makes more accessible to the American worker in Industrial Chemistry the many and various processes proposed for the production of cyanide compounds, and should be a help in stirring him to greater endeavor along these lines.

The Index, rarely found in French books, has been added by the translator, and at his suggestion the publishers have appended Dr. Chas. E. Munroe's brochure on "*Precious Metals Recovered by Cyanide Processes*" which recently appeared as a publication of the U. S. Dept. of Commerce and Labor.

The translator, being moreover interested in Agricultural Chemistry, dares to hope that one of the results of this translation will be the successful fixation of atmospheric nitrogen on an industrial scale.

WASHINGTON, January, 1906.

iii



# TABLE OF CONTENTS.

	PAGE
INTRODUCTION.....	1

## PART ONE.

### CHEMISTRY OF CYANOGEN AND ITS DERIVATIVES.

#### CHAPTER I.

GENERAL CONSIDERATIONS.....	4
-----------------------------	---

#### CHAPTER II.

PHYSICAL AND CHEMICAL STUDY OF CYANOGEN AND ITS DERIVATIVES.....	10
Cyanogen. . . . .	10
Paracyanogen. . . . .	13
Hydrocyanic Acid. . . . .	14
Metallic Cyanides. . . . .	18
Potassium Cyanide. . . . .	20
Sodium Cyanide. . . . .	23
Ammonium Cyanide. . . . .	23
Calcium Cyanide. . . . .	24
Barium Cyanide. . . . .	24
Aluminium Cyanide. . . . .	24
Iron Cyanide. . . . .	25
Chromium Cyanide. . . . .	25
Manganese Cyanide. . . . .	25
Tin Cyanide. . . . .	25
Lead Cyanide. . . . .	25
Copper Cyanide. . . . .	26
Mercury Cyanide. . . . .	26
Silver Cyanide. . . . .	26
Cobalt Cyanide. . . . .	27
Nickel Cyanide. . . . .	27
Gold Cyanide. . . . .	27
Platinum Cyanide. . . . .	27
Double Cyanides. . . . .	28
Ferrocyanides. Potassium Ferrocyanide. . . . .	29
Ferricyanides. . . . .	32



	PAGE
Cobalticyanides.....	34
Manganocyanides.....	34
Platinocyanides.....	34
Aurocyanides.....	35
Nitroprussiates.....	35
Oxygen Compounds of Cyanogen.....	36
Cyanic Acid.....	36
Potassium Cyanate.....	36
Cyanuric Acid and Tricyanates.....	37
Sulphocyanides.....	37
Potassium Sulphocyanide.....	38
Organic Compounds.....	39
Nitriles and Carbylamines.....	39
Cyanic Esters.....	40

### CHAPTER III.

#### GENERAL PROPERTIES AND METHODS OF DETERMINATION OF THE VARIOUS

CYANIDE COMPOUNDS.....	42
I. Analytical Properties.....	42
Hydrocyanic Acid.....	42
Cyanides.....	42
Ferrocyanides.....	43
Ferricyanides.....	43
Sulphocyanides.....	43
Cyanates.....	44
II. Methods for the Analysis of the Various Cyanide Compounds..	44
Cyanides.....	44
Liebig's Method.....	44
Fordos and Gelis' Method.....	45
Analysis of Commercial Potassium Cyanide.....	47
O. Hertig's Process.....	47
Determination of Medicinal Hydrocyanic Acid in Dis-	
tillates of Bitter Almonds and Laurel Cherry (Bui-	
gnet Method).....	48
Ferrocyanides.....	49
Sulphocyanides.....	50
Determination of Ferrocyanides in the Purifying Materials of	
Illuminating-gas.....	50
Knublauch's Method.....	50
Moldenhauer and Leybold's Method.....	51
Burschell's Method.....	52
Zaloziecki's Method.....	52
Donath and Margosches' Method.....	53
Determination of Prussian Blue in the Spent Oxids.....	54
Method of Nauss of the Carlsruhe Gas Works.....	54
Toxicological Research.....	54

## CHAPTER IV.

	PAGE
<b>THERMOCHEMICAL DATA OF THE CYANIDE COMPOUNDS.</b> .....	56
I. Cyanogen.....	56
II. Hydrocyanic Acid. ....	57
III. Potassium Cyanide. ....	58
IV. Ammonium Cyanhydrate. ....	60
V. Potassium Ferrocyanide. ....	60
VI. Potassium Cyanate. ....	66

## PART TWO.

*PRESENT CONDITION OF THE CYANIDE INDUSTRY.*

## CHAPTER V.

<b>COMMERCIAL AND INDUSTRIAL STUDY.</b> .....	69
---	----

## PART THREE.

*METHODS OF MANUFACTURING CYANIDE COMPOUNDS.*

<b>GENERAL CONSIDERATIONS.</b> .....	81
--------------------------------------	----

## CHAPTER VI.

<b>MANUFACTURE OF CYANIDES.</b> .....	85
<b>I. Non-synthetic Processes.</b> .....	85
<b>A. Extraction of Cyanides from Ferrocyanides.</b> .....	85
Old Process.....	85
Liebig's Process. ....	87
Wagner's Process. ....	88
Chaster's Process. ....	88
Rossler and Hasslacher's Process. ....	89
Wichmann and Vautin's Process. ....	90
Dalinot's Process. ....	92
Adler's Process. ....	93
Etard's Process. ....	94
Bergmann's Process. ....	94
<b>B. Extraction of Cyanides from Sulphocyanides.</b> .....	95
<b>I. By Oxidation.</b> .....	96
Raschen's Process. ....	97
Beringer's Process. ....	101
<b>II. By Reduction.</b> .....	102
Playfair's Process. ....	102

## TABLE OF CONTENTS.

	PAGE
Hans Luttke's Process.....	104
British Cyanide Co.'s Process.....	105
Hetherington and Musspratt's Process.....	106
Process of the Silesia Verein Chemische Fabrik....	107
Goerlich and Wichmann's Process.....	107
Bower's Process.....	107
Conroy's Process.....	108
Raschen, Davidson, and Brock's Process.....	110
Etard's Process.....	110
Finlay's Process.....	110
<b>II Synthetic Processes—General Remarks.....</b>	<b>111</b>
<b>A. Processes Utilizing Atmospheric Nitrogen.....</b>	<b>117</b>
Bunsen's Process.....	123
Possoz and Boissière's Process.....	124
Newton's Process.....	126
Blair's Process.....	126
Armengaud's Process.....	126
Marguerite and Sourdeval's Process.....	126
Mond's Process.....	127
Weldon's Process.....	128
Fogarty's Process.....	128
Dickson's Process.....	129
Lambilly's Process.....	129
Gilmour's Process.....	134
Young's Process.....	134
Mackey's Process.....	135
Readmann's Process.....	135
Mehner's Process.....	137
Swan and Kendall's Process.....	137
Pestchow's Process.....	137
Chipmann's Process.....	138
Moise and Mehner's Process.....	140
Castner's Process.....	141
Hornig and Schneider's Process.....	143
Mehner's Process.....	143
Frank and Caro's Process.....	144
Process of the Chemische Fabrik Pfersée, Augsburg.....	149
Berniger, Wolfram and Blackmore's Process.....	150
Dziuk's Process.....	150
Process of the General Electro-Chemical Co.....	152
<b>B. Processes Utilizing Ammonia.....</b>	<b>153</b>
Lance and Bourgade's Process.....	156
Mactear's Process.....	157
Stassfurter Chemische Fabrik's Process.....	158
Moulis and Sâr's Process.....	160
Lambilly's Process.....	161
Beilby's Process.....	162
Young and Macfarlane's Process.....	163

# TABLE OF CONTENTS.

ix

	PAGE
Chaster's Process. ....	165
Pleger's Process. ....	165
Roca's Process. ....	166
Hood and Salamon's Process. ....	169
Hornig's Process. ....	170
Schneider's Process. ....	171
Castner's Process. ....	172
Process of the Deutsche Gold u. Silber Scheide Anstalt. ....	175
Lambilly's Process. ....	178
Martin's Process. ....	179
Glock's Process. ....	179
Huntington's Process. ....	180
Hoyermann's Process. ....	180
Roussin Process. ....	181
Kerp's Process. ....	181
Kellner's Process. ....	182
Grossmann's Process. ....	182
III. Special Processes. ....	183
Process of the Chemische Fabrik Aktiengesellschaft. ....	183
Vidal's Process. ....	184
Bueb's Process. ....	185
Ortlieb and Müller's Process. ....	170

## CHAPTER VII.

MANUFACTURE OF FERROCYANIDES. ....	192
I. Old Processes, Based on the Use of Nitrogenous Organic Substances	193
Calcination or Production of Metal. ....	197
Engler's Apparatus. ....	201
Theory of the Manufacture of Ferrocyanide of Potassium by the	
Old Process. ....	205
Yield. ....	207
Lixiviation and Crystallization. ....	210
Brunquell's Process. ....	210
Karmrodt's Process. ....	211
Conroy's Process. ....	212
Musspratt's Process. ....	212
Goerlich and Wichmann's Process. ....	213
Process of the Castelet Works. ....	213
II. Extraction of Cyanide Compounds from Illuminating-gas and its	
Residues. ....	214
A. Direct Extraction from Gas. ....	229
Knublauch's Process. ....	231
Gasch's Process. ....	232
Rowland's Process. ....	233
Fowles' Process. ....	233
Clauss and Domeier's Process. ....	234
Schroeder's Process. ....	234

	PAGE
Teichmann's Process.....	235
Lewis' Process.....	236
Bueb Process.....	237
Feld's process.....	241
<b>B. Extraction of Cyanogen Compounds from the Ammoniacal</b>	
Liquors.....	242
Pendrie's Process.....	242
Bower's Process.....	243
Lewis' Process.....	243
<b>C. Extraction of Cyanogen Compounds from the Purifying</b>	
Materials.....	245
Gauthier-Bouchar'd's Process.....	248
Valentin's Process.....	256
Harcourt's Process.....	257
Kunheim's Process.....	257
Hempel's Process.....	257
Wolfram's Process.....	257
Donath's Process.....	258
Richter's Process.....	258
Esop's Process.....	258
Marasse's Process.....	258
Holbling's Process.....	259
Lewis' Process.....	259
Mascow's Process.....	259

## CHAPTER VIII.

<b>MANUFACTURE OF FERRICYANIDES.....</b>	<b>261</b>
The Chlorine Process.....	261
Reichardt's Process.....	263
Process of the Bouxvillers Mines.....	264
Dubosc's Process.....	265
Process of the Deutsche Gold und Silber Scheide Anstalt.....	265
Kassner's Process.....	266
Carl Beck's Process.....	267
Williamson's Process.....	267

## CHAPTER IX.

<b>MANUFACTURE OF SULPHOCYANIDES.....</b>	<b>269</b>
Geli's Process.....	270
Deiss and Monnier's Process.....	281
Hood and Salamon's Process.....	282
Brock's Process.....	282
British Cyanides Co.'s Process.....	283
Albright's Process.....	285
Tcherniac Process.....	285
Goerlich and Wichmann's Process.....	286

## TABLE OF CONTENTS.

xi

### CHAPTER X

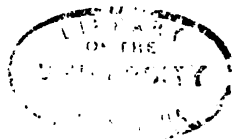
	PAGE
MANUFACTURE OF PRUSSIAN BLUE AND VARIOUS OTHER COMPOUNDS.....	288
Soluble Prussian Blue. ....	292
Turnbull's Blue.....	292
Monthier's Blue or Ammoniacal Prussian Blue.....	292
Antimony Blue. ....	293

### PART FOUR.

#### *THE USE OF CYANOGEN COMPOUNDS.*

CONCLUSIONS.....	321
TABLES AND DATA.....	323
APPENDIX: DIGEST OF U. S. PATENTS RELATING TO CYANIDE PROCESSES FOR THE RECOVERY OF PRECIOUS METALS .....	331
INDEX.....	403





# THE CYANIDE INDUSTRY.

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## INTRODUCTION.

Chemical industries are in a high degree artificial and progressive.

(BERTHELOT: Opening speech at the International Congress of Chemistry, Paris, 1900.)

If the condition of chemical industry at the beginning and at the end of the nineteenth century be compared, one is immediately impressed with the immense progress which has been accomplished.

Chemical industry, at the beginning, being for the most part based on a more or less crude empiricism, could not hope for better results than those brought about either through accident or through long experience.

Gradually, the rational study of reactions, and the adaptation of purely scientific ideas and discoveries to manufacturing, made it necessary to have, as the basis of each *modus operandi*, a profound theoretical knowledge. From that moment advance in industrial chemistry was rapid and to-day, also, it is intimately bound to the progress of scientific research; it is the immediate result of it.

Among the scientific discoveries which have had a great effect on the progress of industrial chemistry, those which especially relate to the synthesis of bodies should be mentioned. It is, in fact, due to synthesis that numerous compounds, which, till then, nature alone was thought capable of producing, have been successfully reproduced. The processes for the manufacture of certain products have been greatly simplified, and consequently the net cost considerably reduced through the industrial adaptation of this principle.



The cyanide industry, which is to be studied in this work, has not escaped this general law.

The happy discovery of Scheele, who was the first to obtain Prussian blue, was the starting-point of this industry. Later, potassium ferrocyanide was prepared by the calcination of nitrogenous materials in the presence of alkali carbonates, and although this *modus operandi* was absolutely empirical, it sufficed, for a long time, for the limited demand. It is probable that this state of affairs would have existed even to-day had not the use of potassium cyanide in the metallurgy of gold given to this industry such an impetus that the manufacture of cyanide compounds has made remarkably rapid development.

The application of cyanides to the treatment of auriferous materials, which dates back about fifteen years, is therefore the immediate cause of the progress realized. Foreseeing the great rôle the new industry was to play, manufacturers and investigators eagerly sought out every improvement possible.

It should, however, be stated that long before not altogether successful attempts had been made to modify the old processes.

In the mean time, the discovery of cyanide compounds in the purifying materials used in the manufacture of illuminating-gas had likewise opened up the field of investigation toward synthetic processes, but only in individual cases, although very interesting in themselves.

The early investigations were unquestionably valuable, and those which relate particularly to synthetic production were the starting-point for many researches. This is the tendency of the times; and either in the hope of a simpler manufacture or of approaching as close as possible to the theoretical side of the question, we shall see that the synthetic processes for the manufacture of cyanides are now preeminent. These are the processes which in all probability should produce the best results, and should solve the problem satisfactorily from an economical as well as an industrial point of view.

The study of this special field of industrial chemistry is therefore of great interest. Having been occupied for many years with the different questions relating thereto, we find no special works on this subject, at least in France.

These reasons led us to bring together in an appropriate didactic order all the documents on this subject which we have been able to collect in the course of our researches; such is the genesis of the work which we present to the public.

The work divides itself into four parts:

Part I. Chemistry of cyanogen and its derivatives.

Part II. The present condition of the cyanide industry.—Commercial and industrial study.

Part III. Methods for the manufacture of cyanide compounds.

Part IV. Application of the various cyanide compounds.

# PART ONE.

## THE CHEMISTRY OF CYANOGEN AND ITS DERIVATIVES.

---

### CHAPTER I.

#### GENERAL LAWS.

By cyanogen combinations is meant all compounds containing the radical CN.

This radical is derived from several sources. It may arise from the direct union of carbon and of nitrogen, which union produces cyanogen CN; or it may arise by addition or substitution from compounds, such as amides, imides, or amines, whose real radical is C or CO.

The radical CN may therefore be related to two classes of compounds: first, to true cyanogen compounds; second, to isomers of the first class, which isomers contain the same elements in quantitative proportions; the former differ, however, from the latter from the point of view of their chemical constitution, and are endowed with different and peculiar properties.

The formation of cyanogen and of its derivatives, its constitution and the determination of its valency have all been the object of much research, and although these various points have not yet been definitely solved, the results of these various studies allow the question to be thus considered: Carbon, a tetratomic element, is saturated by means of the free nitrogen valencies. This latter is sometimes triatomic, and sometimes pentatomic. In the latter case three of its

valencies are different from the other two. It follows that the carbon may therefore satisfy three of its valencies; the compound thus formed will have three free bonds, one attached to the carbon and two to the nitrogen. The constitution of cyanogen may therefore, from these considerations, be represented by the formula  $-C \equiv N =$ .

This constitution of cyanogen allows some of its properties to be at once foreseen. If the nitrogen be replaced by elements of the same atomic value, the original compound becomes transformed into a more carbonaceous one. On the other hand, if the radical CN is connected with an alcoholic radical, the union takes place through the carbon atom. Moreover, Gautier, Wurtz, Limpricht, and Cloez admit that cyanogen is trivalent, for they succeeded in forming the union of hydrocyanic acid and of its esters with the haloid acids. The question of the formation of cyanogen and its compounds is far from being solved. It has been the object of much dispute, and deep study has not given sanction to one theory more than to another.

The various methods by which this formation may be explained are based, rather, on probabilities than upon real data and an exact knowledge of the phenomena produced.

Nevertheless, this question is worthy of attention from more than one point of view. No doubt the discovery of the true method of the formation of the cyanogen compounds would bring about, as an immediate result, the proper process of manufacturing these same compounds. Therefore it may not be useless, at the beginning of this work, to give some idea of the theory of "cyanides," and, without attempting to establish it in a definite manner, to give the pros and cons of each of the theories propounded.

It is known that the radical CN cannot be formed through a direct union; it is formed, however, whenever C and N are found in the presence of an alkali at a high temperature: then there is formed a cyanogen compound in which the group CN is found united to the alkali metal. This reaction takes place according to the general formula



This reaction, or rather the formation of the group CN, may be explained in several ways; in favor of each theory strong but

refutable argument may be presented. The various ways of considering the subject will be treated in order.

Let us take, for example, cyanide of potassium composed of the three elements



the union of which will give the final product CNK, and let us see under which conditions this product may be formed.

Three hypotheses are put forth in explaining this formation.

(1) In the presence of the alkali metal the carbon unites with the nitrogen to form cyanogen CN, which, reacting on the alkali metal as fast as it is formed, would give the cyanide of this metal as end reaction

(2) The nitrogen unites with the alkali metal to form a nitride, which in contact with carbon becomes transformed into cyanide.

(3) First, there is a union of carbon and potassium, forming a carbide, with which nitrogen reacts to produce cyanide.

The first thing noted in these three hypotheses is that in each case the final combination takes place only after an intermediary reaction, and that the fixation of nitrogen cannot take place without this intermediate agent, the nature of which is still undetermined. The first hypothesis is supported by the following facts: When cyanide of potassium is prepared by heating nitrogenous animal matter with an alkali carbonate, it is noticed that the formation of the cyanide takes place only at a temperature in the neighborhood of which the alkali carbonate is reduced to a metallic state. Therefore the combination  $\text{C} + \text{N}$  is due to the presence of the alkali metal.

Schuetzenberger, among others, puts forth the theory that at the temperature of the experiment the carbon tends to become separated from the alkali with which it is combined.

Moreover, if a current of free nitrogen or of ammonia be passed over a mixture of alkali carbonate and charcoal heated to bright redness, there is formation of cyanide. The same result is obtained if nitrogenous matter be heated in the presence of potassium or sodium. All these facts would seem, therefore, to prove that the presence of an alkali metal is necessary to effect the union of carbon with nitrogen. Another corroboration of these observations

is the fact that cyanide of sodium is formed with much more difficulty than cyanide of potassium, a phenomenon which is easily explained, since carbonate of sodium is less easily reducible than carbonate of potassium.

The same would be the result if caustic alkalis were used instead of carbonates. That cyanogen and oxygen can not coexist in the same medium is a known fact; on this account it is necessary first to reduce the oxygen compounds in order to permit the formation of cyanides.

A third remark, no less important, to add to the two preceding ones, is the following: If a current of nitrogen be passed over carbon, heated to redness, and the product of this operation be brought into contact with melted potassium, there will be no formation of cyanide. Against these convincing facts the following objection is brought: if a current of nitrogen be passed over a mixture of charcoal and baryta, heated to a temperature lower than that necessary for the reduction of the base, there will be formed a cyanide of barium without there having been a previous formation of metallic barium.

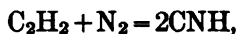
The rôle played by the metal would therefore seem to be destroyed, and the statement just made leads immediately to the discussion of the two other hypotheses: formation of a nitride or of a carbide.

Although experiments have not yet clearly proven that the formation of cyanides is possible by means of the intermediate passage through a nitride, yet this method of formation is explicable. Moissan, who prepared nitride of calcium, was enabled, however, by bringing this body in contact with charcoal, to obtain only very small quantities of cyanide.

Finally, it is a fact well known that by the action of nitrogen on the carbides of the alkaline earths, these become transformed into cyanides. This phenomenon may explain the formation of barium cyanide mentioned above.

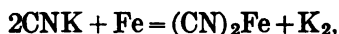
It is not at all improbable that the same reaction takes place with the carbides of the alkali metals, although thus far no real experimental data prove it. It still remains to mention Berthelot's hypothesis, a theory quite closely related to that of the carbides. This investigator, having observed that nitrogen and acetylene unite

directly under the influence of the electric spark, exploding in a mixture of these gases diluted with hydrogen:

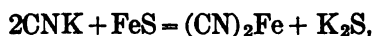


supposes that the formation of cyanides is preceded by that of the acetylide,  $\text{C}_2\text{K}_2$ , which, like acetylene, would unite with nitrogen.

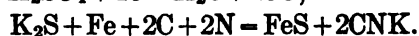
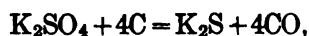
This question is far from being solved. It is only by means of thermochemical studies of the various phenomena which control these combinations that a clear and exact idea of the conditions under which they are formed will be attained. It is to be hoped that modern investigators may solve this problem; this would be the cause of great progress for the manufacture of cyanide compounds. The theory of the formation of ferrocyanide is no better known. In its preparation, by means of nitrogenous substances in the presence of potassium carbonate, a cyanide would be formed according to one of the reactions mentioned above, i.e., there would be formation of cyanogen, reduction of the carbonate to a metallic state, and reaction of the cyanogen on the metal to form cyanide of potassium. The rôle which iron plays is unknown; all that is known is that the ferrocyanide is formed only during lixiviation, yet it is necessary that iron be present. The reaction takes place according to the following equations:



or



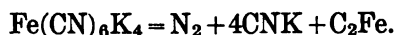
The presence of sulphide of iron is explained as follows: Commercial potassium carbonate always contains a certain amount of sulphate. This sulphate being subjected to the action of charcoal and iron, at a high temperature, generates sulphide of iron according to the following equation:



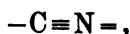
In his treatise on "Médicaments chimiques," Prunier puts forth another theory. According to him, nitride of carbon, which is produced by calcining animal substances, would react on potassium carbonate in order to form acetylene. This gas would unite with the potassium set free and with the nitrogen of the nitrogenous substance, or with nitrogen of the atmosphere, according to the following equation:



when the iron would, in its turn, react to form cyanide of iron, which, according to the reaction above cited, would become transformed into ferrocyanide. It is definitely known that the ferrocyanide is not formed during the calcination, for at that temperature the ferrocyanide would be decomposed, giving off nitrogen and forming bicarbide of iron and potassium cyanide, according to Liebig's theory:



The formation of sulphocyanides, which is readily produced, is easily understood because cyanogen remains an unsaturated body, as the following formula shows:



the sulphur, which is bivalent, saturating two of the free atoms, while the alkali metal saturates the last. A like reasoning may explain the formation of cyanates, the bivalent oxygen of the cyanates replacing the sulphur of the sulphocyanides.

To sum up the study of the union of carbon with nitrogen is interesting from more than one point of view, because of the very difficulty which controls its formation and from the numerous bodies to which it may give rise, bodies of which a general study will now be made.



## CHAPTER II.

### CHEMICAL AND PHYSICAL STUDY OF CYANOGEN AND ITS DERIVATIVES.

CYANOGEN,  $C_2N_2$ , = 52.

$$100CN = \begin{cases} C = 46.15 \\ N = 53.85 \end{cases}$$

---

$$100.00$$

THE formula of cyanogen is  $N \equiv C - C \equiv N$ . It is really a nitride of carbon.

It was discovered in 1814 by Gay-Lussac, who gave it this name because it formed part of the composition of Prussian blue (*χυαρος*) blue, (*γενναω*) to generate.

This discovery exerted considerable influence on the progress of chemistry, and on the theories at that time admitted. The investigations of Gay-Lussac upon this body which he had just discovered set forth, in fact, that this compound, because of its properties, resembles greatly the halogens, and that in many reactions it behaves like a simple substance, i.e., it plays the rôle of an element. In fact cyanogen is oftentimes represented by the simple formula Cy, instead of CN.

Cyanogen is a colorless gas, with an odor reminding one of bitter almonds. It exerts a decidedly irritating action on the mucous membrane, and may in some cases even cause the eyes to water.

It has a density of 1.8064, when compared with air, or 25.533 ( $H=1$ ). One liter weighs 2.235 grams.

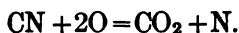
One volume of water at  $20^\circ C$ . dissolves  $4\frac{1}{2}$  times its volume of gas, whereas alcohol dissolves 25 times its volume.

It becomes a liquid at  $20.7^\circ C$ . under ordinary pressure, and at

15° C. under a pressure of 4 to 5 atmospheres. This liquid is transparent and mobile, with a density of 0.866.

The evaporation of this liquid in open air causes such a lowering of temperature that the portion not evaporated becomes solid. Solid cyanogen melts at -34° C.

Cyanogen gas burns in air with a purple flame, producing nitrogen and carbonic acid:



It is readily decomposed by heat. Its formation is endothermic, and that is the reason why it cannot be obtained by the direct union of carbon and nitrogen.

The electric spark breaks it up into its elements; a mixture of 1 vol. of cyanogen and 2 vols. of oxygen explodes under the influence of the electric spark into 1 vol. of nitrogen and 2 vols. of carbonic acid.

An aqueous solution of cyanogen becomes quickly altered in the light; a black flocculent precipitate, called azulmic acid,  $\text{Cy}^n(\text{H}_2\text{O})^n$  or  $\text{C}_4\text{H}_4\text{N}_4\text{O}_2$ , separates out, caused by the union of 4 equivalents of water and 4 equivalents of cyanogen, while in the solution there remain carbonic anhydride, hydrocyanic acid, ammonia, urea, and ammonium oxalate (Woehler).

The same result is observed in an alcoholic or ether solution. The presence of an acid suffices to prevent these transformations. The same substances are produced in an ammoniacal solution as in an aqueous solution.

Cyanogen does not unite directly with hydrogen. If a mixture of equal volumes of cyanogen and hydrogen be passed in a tube heated to 500° C., only traces of hydrocyanic acid are obtained.

On the other hand, cyanogen unites with nascent hydrogen, producing ethylene diamine; finally, if sealed tubes heated to 500° C. are employed, the union of the two gases is complete.

Cyanogen does not unite directly with chlorine, even in the light; but if the two gases are moist, an oily liquid and a solid aromatic substance are formed.

On the other hand, cyanogen is decomposed by hypochlorous anhydride, and by hypochlorous acid, with formation of carbonic acid, chlorine, nitrogen, and gaseous cyanogen chloride.

It does not unite directly with sulphur, but when cyanogen and hydrogen sulphide are brought together in a moist state two crystallizable compounds are formed, a monosulphydrate and a bisulphydrate of cyanogen, corresponding respectively to the formulas  $C_2N_2 \cdot SH_2$  and  $C_2N_2 \cdot (H_2S)_2$ . The mono- or the bisulphydrate is obtained according as an excess of cyanogen or of hydrogen sulphide is used.

In a heated state, cyanogen absorbs potassium, with formation of potassium cyanide. An aqueous solution of potash absorbs the gas energetically, with formation of azulmate of cyanide, cyanate and oxalate of potassium.

It combines directly with zinc, with cadmium at  $300^\circ C.$ , and with lead at  $500^\circ C.$  Heated to redness with iron, the latter absorbs the carbon, setting the nitrogen free, the metal becoming brittle. With the other metals it unites only indirectly.

Some organic bases may unite with it, e.g., aniline, toluidine, codeine, producing cyaniline, cyanotoluidine, cyanocodeine, respectively, bodies which may be decomposed by an alkali with formation of oxalic acid or its derivatives. Cuprous chloride absorbs it. It is decomposed by manganic sulphate, which reduces it to carbonic acid and nitrogen. Mercurous oxide absorbs it slowly.

Potassium carbonate, heated to redness, absorbs cyanogen, with production of cyanide and cyanate of potassium.

Properly stated, cyanogen does not exist *free*. Yet, in certain cases it is found in small quantities, as, for example, in the gases of the blast-furnace, where one finds as much as 1.34%. It is also formed when a mixture of illuminating-gas and ammonia is burned in a Bunsen burner.

It is formed, indirectly, in the following reactions:

(1) When nitrogenous animal substances are burned in presence of an alkali carbonate, particularly potassium carbonate.

(2) When nitrogenous animal substances are burned in the presence of potassium.

(3) When nitrogen acts on a mixture of charcoal and potash.

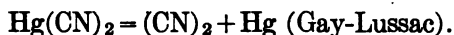
(4) When ammonia acts on charcoal, heated to redness.

In these reactions, however, it is always combined; and it is as a cyanide of potassium, sodium, or ammonium that it may be extracted. These methods of formation constitute the base of the

process of the manufacture of alkali cyanides, of which more in a later chapter.

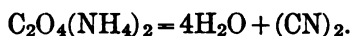
Cyanogen may be prepared by various methods.

(1) By heating dry mercuric cyanide to dull redness in a retort:



(2) By heating in a retort an intimate mixture of 2 parts potassium ferrocyanide and 3 parts of mercuric chloride (Kemp).

(3) By the dry distillation of ammonium oxalate or of oxamide:



(4) By heating glycerine and ammonium oxalate at 200° C. (Storch).

(5) By heating, on an oil-bath at 160–170° C., a dry mixture of zinc cyanide and cupric chloride, there is formed cupric cyanide which, under the influence of heat, loses one half of its cyanogen, and becomes transformed into cuprous cyanide and cyanogen.

It is likewise produced by heating, under the same conditions, a solution of copper sulphate into which a concentrated solution of potassium cyanide is gradually poured (Varet)

Finally, cyanogen is formed with an absorption of heat—38 calories, when carbon in the state of the diamond is used:



#### PARACYANOGEN $(\text{CN})_n$ .

This is a polymeric modification or an isomer of cyanogen, which is always produced in the preparation of cyanogen by the decomposition of the cyanides of mercury or of silver by heat, the amount of paracyanogen increasing in proportion as the temperature is low.

It is also obtained by heating cyanogen in a closed vessel; but, on the other hand, when paracyanogen is likewise heated out of contact with air it is decomposed into cyanogen. However, when the vapor of cyanogen exerts a definite pressure on the paracyanogen remaining, the production of the former ceases. This tension of transformation varies proportionally with the temperature, but it is constant for a given temperature.

Troost and Hautefeuille determined the conversion tension of cyanogen:

Temperature.	Tension of Transformation.	Temperature.	Tension of Transformation.
502	54 mm.	599	275 mm.
559	125 "	601	318 "
575	129 "	620	868 "
587	157 "	640	1310 "

This is therefore a phenomenon quite analogous to that of the allotropic transformation of white phosphorus into red phosphorus.

Paracyanogen is a brownish-black powder, insoluble in water, soluble in concentrated sulphuric acid. It becomes converted into cyanogen on heating in a current of inert gas, such as carbonic acid or nitrogen.

#### HYDROCYANIC ACID (PRUSSIC ACID), $\text{CNH} = 27$ .

$$100\text{CNH} = \begin{cases} \text{C} = 44.44 \\ \text{N} = 51.85 \\ \text{H} = 3.71. \end{cases}$$


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$$100.00$$

Hydrocyanic acid or nitride of formic acid has the formula  $\text{CNH}$ . It is also called prussic acid. It was discovered by Scheele in 1782, but Gay-Lussac was the first to obtain it in a pure state, in 1811, and to establish its composition. It was known to Egyptian priests, who used it in the killing of traitors.

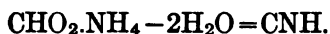
It occurs in certain plants; in the leaves of the laurel-cherry and the laurel-leaf willow, in the leaves and blossoms of the peach, and in bitter almonds. The kernels of most of the stone-fruits contain some. The root of *Jatropha Mannihot* also contains it, from which it may be obtained by distillation with water.

It is produced by the breaking up of the amygdalin, a neutral substance found in various plants, by the action of water.

It is the hydrocyanic acid which gives to liquors prepared with almonds their characteristic odor and flavor.

Hydrocyanic acid is sometimes obtained in the distillation of nitrogenous products, and in the oxidation of certain organic substances with nitric acid.

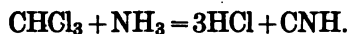
Formate of ammonium heated to 200° C. loses water and forms hydrocyanic acid:



The action of the electric spark on a mixture of acetylene and nitrogen gives hydrogen cyanide:

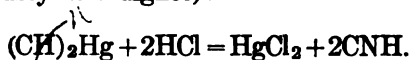


When an electric furnace is started, a perceptible odor of laurel-cherry, due to hydrocyanic acid, is noticed. This is produced by the union of atmospheric nitrogen with acetylene, which latter is formed by the union of the carbon of the electrodes with the hydrogen due to the decomposition of water-vapor by the voltaic arc. Hydrogen cyanide is also produced by the action of chloroform on ammonia:



It is likewise produced in appreciable quantities in the combustion of a mixture of air and nitrogen dioxide in an inverted Bunsen burner; likewise in tobacco-smoke; and by the passage of an electric discharge in 9% aniline; and in the electric arc

To obtain it pure, mercuric cyanide is, as a rule, decomposed by hydrochloric acid (Gay-Lussac) when there is formed hydrocyanic acid and corrosive sublimate; but, on account of the affinity of this salt for hydrocyanic acid, the yield is rather small. This can be remedied by the addition of ammonium chloride, which unites with the sublimate (Bussy & Buignet):



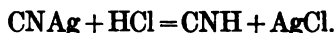
The best procedure consists in treating potassium ferrocyanide with sulphuric acid (15 parts ferrocyanide, 7 sulphuric acid, 9 water). The gas first passes over calcium chloride, and is then collected in a cylinder surrounded by a cooling mixture. In this way the anhydrous acid is obtained. To obtain the aqueous acid, it is only necessary to distil the mixture:



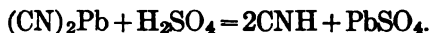
Several other processes have been brought out:

Clarke's process, which consists in adding 4 parts of potassium cyanide to a solution of 9 parts of tartaric acid in 60 parts of water. In this case cream of tartar separates out, leaving a supernatant liquid of hydrocyanic acid.

Everitt's process is based on the decomposition of silver cyanide by hydrochloric acid:

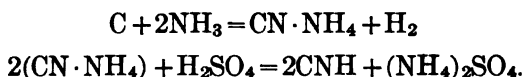


Thompson's process is based on the decomposition of lead cyanide by sulphuric acid:



Vauquelin's process consists in passing a current of hydrogen sulphide over very dry mercuric cyanide.

Kuhlmann's process is likewise of interest. Dry ammonia gas is passed through a glass tube filled with pieces of charcoal, and heated to redness. The gas formed is conducted through dilute sulphuric acid at  $50^\circ \text{C}.$ , and then into a cooled receiver. Ammonium cyanide is formed, which in contact with sulphuric acid forms ammonium sulphate and hydrocyanic acid:



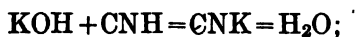
The anhydrous acid is a colorless liquid of specific gravity 0.7058 at  $7^\circ \text{C}.$ , and 0.6969 at  $18^\circ \text{C}.$  It becomes a solid at  $-15^\circ \text{C}.$ , boils at  $26.5^\circ \text{C}.$  Its vapor density is 0.9467.

Its odor is characteristic of bitter almonds. It is soluble, or rather miscible with water and alcohol in all proportions. The density of its aqueous solutions decreases in proportion as the amount of acid in solution increases. Thus a 1% solution has a specific gravity of 0.9988, while a 16% solution has a specific gravity of only 0.9570. Its aqueous solution is a union. In fact, if equal parts of the two bodies be mixed, a loss of 25% in vapor-tension is produced. When dry, it burns in air with a white flame tinged with violet, with formation of water, carbonic acid, and nitrogen:

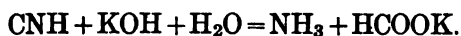


It decomposes rapidly in the light, yielding ammonia and a brown deposit.

The presence of a small quantity of mineral acid renders it more stable. A trace of ammonia decomposes it very rapidly. Concentrated mineral acids transform it very quickly by fixing 2 molecules of water into formic acid and ammonia. Dilute alkalis, in the cold, produce, with it, the corresponding cyanides:



but when boiled, or with concentrated alkalis, there is a formation of alkali formate and ammonia:



It is likewise decomposed by chlorine and bromine, yielding hydrochloric acid, hydrobromic acid, and crystalline compounds, such as hydrochloride and hydrobromide of cyanogen.

In the presence of slightly warmed potassium it yields potassium cyanide.

Nascent hydrogen reduces it to methylamine:



Heat breaks it up into hydrogen, cyanogen, nitrogen, and carbon. The electric spark decomposes it nearly completely only when it is mixed with hydrogen, or when it is in an aqueous solution.

Manganese dioxide absorbs gaseous hydrocyanic acid entirely when mixed with hydrogen. It is a weak acid which does not decompose carbonates. It is formed by the union of equal volumes of hydrogen and cyanogen without condensation.

*Action on the System.*—Prussic acid is the most violent and rapid poison known. A dose of 5 centigrams suffices to kill a man. One drop of this acid placed on the tongue of a dog renders him instantly unconscious. Scheele, the discoverer of hydrocyanic acid, himself died, poisoned by it. Scharinger, a chemist of Vienna, died in two hours, the result of letting two drops of this acid fall on his arm.

Its vapors are likewise extremely poisonous. Their respiration causes violent headaches, nausea, pains, and oppression in the chest.

In gold-mines where the cyanide process is in use, workmen



whose duty it is to clean the vats are affected with general weakness, headaches, dizziness, and nausea. Often a kind of eruption, especially on the arms, breaks out in them. These eruptions may be readily overcome by internal and external application of potassium ferrocyanide.

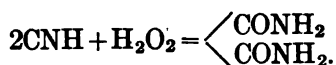
Prussic acid seems to affect the circulatory rather than the nervous system; it destroys muscular sensibility, and death results through suspension of the heart's action.

Quite often the victim is seized, before death, by violent attacks of tetanus.

Properly speaking, there is no antidote for prussic acid. Inhalation of chlorine and of ammonia have been advised, but ammonium cyanide and cyanogen chloride are themselves just as poisonous.

If these bodies have sometimes produced favorable effects, these must rather be attributed to an excitation of the nervous system. Likewise, internal application of essence of turpentine (30 grams in emulsion by spoonful) have been advised. The affusion of cold water on the spinal column and on the base of the skull are recommended.

Robert and Krohl have quite recently praised the use of hydrogen peroxide as an antidote for prussic acid. A 30% solution is used internally, and a 3% solution for subcutaneous injections. The following reaction takes place: the hydrocyanic acid, reacting with hydrogen peroxide, is changed into oxamide, which is non-poisonous:



This method has been quite successfully used in the English gold-mines for the past four years, and in many cases subcutaneous injection suffices. Dr. Aulst of the Austria-Hungary Medical Association (June 2, 1894) recommended the use of cobalt nitrate. This salt forms with potassium cyanide an insoluble and harmless compound.

#### METALLIC CYANIDES.

By its union with metals, hydrocyanic acid forms cyanides or cyanhydrates, salts which are analogous to chlorides, bromides, and iodides.

Cyanides may be divided into two classes, simple and double cyanides.

The simple cyanides, especially the alkali cyanides, are formed in many reactions:

(1) By the action of cyanogen or of gaseous hydrocyanic acid on the slightly heated metal.

(2) By heating carbonates or hydrates of alkalis in a current of cyanogen.

(3) By double decomposition of hydrocyanic acid and metallic hydrates.

(4) By the action of a current of nitrogen upon a mixture of charcoal and hydrate or carbonate of an alkali.

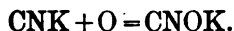
(5) By the ignition of nitrogenous organic substances in the presence of alkalis, hydrates or carbonates, nitrites or nitrates.

(6) By the action of ammonia-gas upon charcoal, heated to redness, or of carbon monoxide upon ammonia, likewise at a red heat:



As to the other cyanides, they are generally obtained by the double decomposition between a metallic salt and an alkali cyanide.

*Properties.*—The cyanides of the alkali metals and of the alkaline earth metals are soluble in water and in alcohol, with formation of a strong alkaline solution; the cyanides of the other metals are insoluble, excepting mercuric cyanide. The cyanides of the alkalis and of the alkaline earths are not decomposed by heat, in the absence of air; but in contact with oxygen they are transformed into cyanates:



The other cyanides are decomposed by heat. In the presence of water and of heat they are all decomposed. Cyanides of the heavy metals give carbon monoxide, carbon dioxide, ammonia, carbon, and the metal; the other cyanides give formates and ammonia.

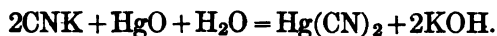
Cyanides have reducing properties. They reduce metallic oxides, being themselves transformed into cyanates.

Mineral acids, e.g., hydrochloric, sulphuric, decompose them,

setting free hydrocyanic acid. Nitric acid decomposes them into nitrates, carbonic acid, and nitrogen:



When the oxides of the heavy metals are digested with a solution of an alkali cyanide, a large part of them is converted into cyanides, whereas the alkali metal becomes hydrated:



They unite with the metallic chlorides, bromides, iodides, nitrates, and chromates.

POTASSIUM CYANIDE, CNK=65.

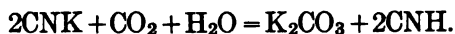
$$100\text{CNK} = \begin{cases} \text{C} = 18.46 \\ \text{N} = 21.54 \\ \text{K} = 60.00 \end{cases}$$


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$$100.00$$

Potassium cyanide, KCN=65, is a white substance having an acrid and slightly bitter taste, leaving an after-taste of hydrocyanic acid. It has a strong, penetrating odor which is characteristic. It crystallizes in anhydrous octohedrons, which are easily fusible and deliquescent. It has an alkaline reaction. It is volatile at a white-red heat without decomposition. It is easily soluble in cold, more so in boiling water (100 parts boiling water dissolve 122 parts), slightly soluble in strong alcohol. Its solubility in alcohol increases in proportion as the alcohol is diluted.

When in solution, or even in a moist state, it is acted upon by carbonic acid, with formations of hydrocyanic acid and potassium carbonate:



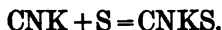
This reaction is of great importance from the manufacturing standpoint; for it shows how little stable that body is, and the means necessary to be taken to prevent its decomposition and to keep it intact.

When its aqueous solution is heated to boiling out of contact with air, it breaks up into potassium formate and ammonia. In this way it may be completely decomposed.

Dry carbonic acid like dry air does not react on dry potassium cyanide. It is easily oxidized, which means that it is an energetic reducing agent. When burned in air, or with manganese dioxide, or with iron oxide, it is converted into a cyanate. This property was the cause of its being used in the reduction and separation of certain metallic oxides; it has the advantage over other reducing agents of not carburetting the metal. This reaction takes place generally at temperatures only slightly raised. It is likewise oxidized by chloride of lime, which converts it into cyanate of lime. When its aqueous solution is treated by an electric current it is converted into cyanate.

It also works as a reducing agent in a wet way.

When fused with sulphur it is changed into sulphocyanide:



This same result is obtained when it is fused with sulphide of tin or of antimony.

Its aqueous solution dissolves several metallic oxides, and even metals; e.g., copper, zinc, nickel, iron. Mercury, platinum, tin are not dissolved by it; cadmium, silver, gold are dissolved by it, but only in contact with air. This last property is of the greatest importance, for to it is due the development of the manufacture of the alkali cyanides. Likewise, chloride of silver, selenium, tellurium, and iodine are dissolved by it. In the case of iodine there is formed cyanogen iodide, or a double iodide of cyanogen and potassium.

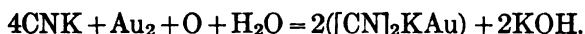
Heated with nitrate or chlorate of potassium a violent explosion takes place. When potassium sulphate is fused with potassium cyanide, the latter becomes converted into cyanate of potassium, and there is also formed potassium sulphide. When hydrogen sulphide is passed through a concentrated aqueous solution of potassium cyanide, an intense red coloration results, with formation of yellow needles of chryseane,  $\text{C}_4\text{H}_5\text{H}_3\text{S}_2$ .

When sulphurous acid is passed through a cooled 40% solution of potassium cyanide hydrocyanic acid is set free, the solution becomes brown, and in a few days there are formed crystals of cyanosulphite of potassium,  $\text{SO}_2\text{CNK} + \text{H}_2\text{O}$ , a solution which possesses

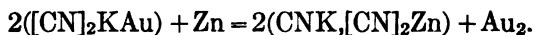
the property of reducing salts of gold and silver. When this solution is treated with acids there is formed acid-cyanosulphite of potassium, which is only slightly soluble and decomposable by heat.

Potassium cyanide is decomposed by permanganate of potash.

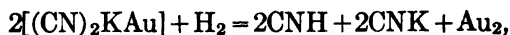
The most remarkable and interesting property of potassium cyanide is that of dissolving gold in the presence of the oxygen and moisture of the atmosphere, since this property is the cause of its extensive use in industry. This solution takes place according to the following reactions:



When treated with zinc, this new compound yields metallic gold, with formation of a double cyanide of zinc and potassium:



In reality the reaction takes place in another way; at least it is explained in the following manner: Zinc causes the formation of a voltaic couple, and in general, where the solution contains potassium-gold-cyanide and cyanide of potassium in excess, and zinc, the following reactions take place:



Not its least interesting property is that of dissolving certain metallic sulphides, such as those of copper, silver, gold, zinc, iron, which may be used in metallurgy.

Finally, it possesses extremely toxic properties. Two centigrams of this salt suffice to cause the death of a man.

In case of poisoning by this compound, the following treatment is recommended: Cause the patient to breathe chlorinated water, liquor of Labarraque, or ammonia; administer doses of essence of turpentine (30 grams in emulsion) or multiple antidote of Jeannel; affusions of cold water on the head, anodynes, and tonics.

CYANIDE OF SODIUM  $\text{CNNa} = 49$ .

$$100\text{CNNa} = \begin{cases} \text{C} = 24.49 \\ \text{N} = 28.57 \\ \text{Na} = 46.94 \end{cases}$$


---


$$100.00$$

It corresponds to the formula  $\text{CNNa} = 49$ .

It is formed in the same way as is potassium cyanide. Its properties are almost identical. It is rather difficult to obtain it in crystalline form, for its aqueous solution evaporates in a mass. The only important difference between sodium and potassium cyanide is that the former contains more cyanogen, which is to its advantage. For example, the atomic weight of  $\text{CNNa}$  is 49, of which 26 is cyanogen, i.e., 53%, while the atomic weight of  $\text{CNK}$  is 65, of which 26 is cyanogen, or only 40%.

On account of the progress of electrochemistry in preparing metallic sodium in large quantities and at a moderate price, sodium cyanide is daily becoming of greater importance.

Yet the use of potassium cyanide is preferred in industry, because it is not deliquescent and therefore may be more easily transported. At present a double cyanide of sodium and potassium is being prepared  $(\text{CN})_2\text{NaK}$ , which makes possible the use of a larger quantity of free cyanogen under a less weight.

AMMONIUM CYANIDE,  $\text{CN} \cdot \text{NH}_4 = 44$ .

$$100\text{CN} \cdot \text{NH}_4 = \begin{cases} \text{C} = 27.27 \\ \text{N} = 63.63 \\ \text{H} = 9.10 \end{cases}$$


---


$$100.00$$

Ammonium cyanide or cyanhydrate of ammonia,  $\text{CN} \cdot \text{NH}_4 = 44$ , is a solid, colorless product crystallizing in cubes or quadrangular prisms. It has an alkaline reaction, and an odor reminding one of both hydrocyanic acid and ammonia. It is readily soluble in water and alcohol, and quite unstable in air, especially when heated. At  $36^\circ \text{C}$ . it undergoes partial volatilization and is converted into azulmic acid. Its vapors are inflammable. It is very poisonous.

It may be prepared as follows:

(1) By the action of ammonia on charcoal heated to redness

if the product of the reaction be collected in a cylinder surrounded by a freezing mixture:



(2) By the double decomposition of ammonium chloride and the cyanides of potassium or of mercury, or ferrocyanide of potassium. Ammonium cyanide exists already formed, as will be seen later, in illuminating-gas

CALCIUM CYANIDE,  $\text{Ca}(\text{CN})_2$ , = 92.

$$100\text{Ca}(\text{CN})_2 = \begin{cases} \text{C} = 26.09 \\ \text{N} = 30.43 \\ \text{Ca} = 43.48 \end{cases}$$


---

100.00

It occurs as anhydrous crystalline cubes, soluble in water. Its solution is decomposed by heat and carbonic acid. It is prepared by the action of hydrocyanic acid on a solution of lime or on milk of lime.

BARIUM CYANIDE,  $\text{Ba}(\text{CN})_2$ , = 189.

$$100\text{Ba}(\text{CN})_2 = \begin{cases} \text{C} = 12.70 \\ \text{N} = 14.81 \\ \text{Ba} = 72.49 \end{cases}$$


---

100.00

It is obtained by heating ferrocyanide of barium in a closed tube (Berzelius), or by saturating baryta water with hydrocyanic acid (Ittner), or, still more easily, by the action of nitrogen upon a mixture of charcoal and of baryta heated to redness (Margueritte and Sourdeval). This last reaction has been applied industrially.

It is soluble in water and in alcohol and is decomposed by heat. For a long time its use has been praised in metallurgy for the cementation of steel.

ALUMINUM CYANIDE.

This is not yet known.

CYANIDE OF ZINC,  $\text{Zn}(\text{CN})_2$ , = 117.

$$100\text{Zn}(\text{CN})_2 = \begin{cases} \text{C} = 20.51 \\ \text{N} = 23.93 \\ \text{Zn} = 55.56 \end{cases}$$


---

100.00

It is a white substance, insoluble in water and in alcohol, soluble in the alkali cyanides with formation of double cyanides. It is prepared either by the double decomposition of zinc sulphate and potassium or ammonium cyanide, or by the action of hydrocyanic acid on the acetate or hydrate of zinc.

#### IRON CYANIDES.

The simple cyanides of iron are little known, because of the extreme ease with which they are transformed into the complete cyanides.

Two of them are known from which a whole series of double salts are derived: they are ferrous cyanide,  $\text{Fe}(\text{CN})_2$ , and ferric cyanide,  $\text{Fe}_2(\text{CN})_6$ . The ferrocyanides correspond to the former, while the ferricyanides are derived from the latter.

#### CHROMIUM CYANIDES.

Chromous cyanide,  $\text{Cr}(\text{CN})_2$ , is white. It is obtained by precipitating a solution of chromous chloride with potassium cyanide. It is soluble in an excess of potassium cyanide and is easily changed in the air, giving oxide of chromium and chromic cyanide. Chromic cyanide,  $\text{Cr}_2(\text{CN})_6$ , is more stable; it is obtained by precipitating at the boiling-point a solution of chromic chloride with an excess of potassium cyanide. These two cyanides form respectively chromous and chromic cyanides, analogous to ferrous and ferric cyanides.

#### CYANIDE OF MANGANESE.

Only the double cyanides are known, Manganous and manganic cyanides, which will be studied later.

#### CYANIDE OF TIN.

This is unknown in a free state.

CYANIDE OF LEAD,  $\text{Pb}(\text{CN})_2$ , -258.

$$100\text{Pb}(\text{CN})_2 = \begin{cases} \text{C} = 9.30 \\ \text{N} = 10.85 \\ \text{Pb} = 79.85 \end{cases}$$


---

100.00



It is but imperfectly known. When prepared by the action of ammonium cyanide and lead acetate it is yellow, while, when it is obtained by the addition of hydrocyanic acid to an ammoniacal solution of lead subacetate it is white. Kugles gives it the formula  $\text{Pb}(\text{CN})\text{OH}$ , while Erlenmeyer designates it by  $\text{Pb}(\text{CN})_2 \cdot 2\text{PbO}$ .

CYANIDE OF COPPER,  $\text{Cu}_2(\text{CN})_2$ , -178.

$$100\text{Cu}_2(\text{CN})_2 = \begin{cases} \text{C} = 13.49 \\ \text{N} = 15.73 \\ \text{Cu} = 70.78 \end{cases}$$


---

100.00

Cuprous cyanide,  $\text{Cu}_2(\text{CN})_2$ , only is stable. It is a white powder which is precipitated by the action of hydrocyanic acid on an hydrochloric acid solution of cuprous chloride

CYANIDE OF MERCURY,  $\text{Hg}(\text{CN})_2$ , -252.

$$100\text{Hg}(\text{CN})_2 = \begin{cases} \text{C} = 9.52 \\ \text{N} = 11.11 \\ \text{Hg} = 79.37 \end{cases}$$


---

100.00

Mercuric cyanide,  $\text{Hg}(\text{CN})_2$ , only is known. It crystallizes in opaque, colorless prisms soluble in water, insoluble in alcohol. It is prepared by dissolving mercuric oxide in hydrocyanic acid, or by boiling one part of potassium ferrocyanide, two parts of mercuric sulphate, with eight parts of water. It is decomposable by heat, concentrated acids, bromine, iodine, and chlorine (under the influence of solar rays). It is very poisonous.

CYANIDE OF SILVER,  $\text{Ag}(\text{CN})$  = 134.

$$100\text{Ag}(\text{CN}) = \begin{cases} \text{C} = 8.96 \\ \text{N} = 10.44 \\ \text{Ag} = 80.60 \end{cases}$$


---

100.00

It is a white substance, closely resembling silver chloride. It is obtained by precipitating a solution of silver nitrate with potassium cyanide. It is soluble in ammonia, and in hot, concentrated nitric acid, and in the alkali cyanides and chlorides.

CYANIDE OF COBALT,  $\text{Co}(\text{CN})_2$ , -111.

$$100\text{Co}(\text{CN})_2 = \begin{cases} \text{C} = 21.63 \\ \text{N} = 25.22 \\ \text{Co} = 53.15 \end{cases}$$


---

100.00

Cobaltous cyanide,  $\text{Co}(\text{CN})_2$ , is a flesh-colored precipitate, obtained by precipitation of a cobalt salt with potassium cyanide. Oxygen of the atmosphere changes it rapidly.

CYANIDE OF NICKEL,  $\text{Ni}(\text{CN})_2$ , -111.

$$100\text{Ni}(\text{CN})_2 = \begin{cases} \text{C} = 21.63 \\ \text{N} = 25.22 \\ \text{Ni} = 53.15 \end{cases}$$


---

100.00

It is an apple-green substance obtained by precipitating a salt of nickel with potassium cyanide, or by the action of hydrocyanic acid on nickel acetate. It crystallizes with 3 molecules of water.

CYANIDE OF GOLD,  $\text{Au}(\text{CN})_3$ , -222.

$$100\text{Au}(\text{CN})_3 = \begin{cases} \text{C} = 5.41 \\ \text{N} = 6.31 \\ \text{Au} = 88.28 \end{cases}$$


---

100.00

Aurous cyanide,  $\text{Au}(\text{CN})_3$ , is a beautiful pale-yellow crystalline powder, very stable, insoluble in water, alcohol, and acids. It is odorless and tasteless. Heat decomposes it into cyanogen and gold. Boiling potash decomposes it slowly into potassium gold cyanide and metallic gold, soluble in ammonium sulphhydrate, ammonia, and sodium hyposulphite.

CYANIDE OF PLATINUM,  $\text{Pt}(\text{CN})_4$ , -249.

$$100\text{Pt}(\text{CN})_4 = \begin{cases} \text{C} = 9.64 \\ \text{N} = 11.24 \\ \text{Pt} = 79.12 \end{cases}$$


---

100.00

Platinous cyanide,  $\text{Pt}(\text{CN})_2$ , is greenish yellow, insoluble in-

water, acids, and alkalis. It burns in air, leaving a residue of metallic platinum.

### DOUBLE CYANIDES.

Most of the cyanides are capable of combining together to form double cyanides. Often they are produced by dissolving a simple insoluble cyanide in a soluble alkali cyanide.

There are two classes of double cyanides, the stable and the unstable.

The unstable double cyanides are decomposed by dilute acids, when the insoluble cyanide is precipitated and hydrocyanic acid set free; the gas set free results from the action of the acid used on the existing alkali cyanide.

The stable cyanides, on the other hand, resist the action of dilute acids. In this case there is only a substitution of the hydrogen for the potassium (potassium cyanide is the one usually employed), and there is formed a double cyanide of hydrogen and heavy metal.

Salt solutions of nearly all metals, acting on double cyanides, produce the phenomenon of double decomposition.

On account of these differences, the unstable cyanides are generally considered as true double cyanides, i.e., formed by two simple cyanides, while, on the other hand, the stable cyanides are the result of the union of an alkali metal with the radical formed when cyanogen combines with the heavy metal.

This hypothesis seems to be verified from the following: In the stable double cyanides the heavy metal (by heavy metal is meant all metals except alkali and alkaline earth metals) cannot be released by its ordinary reactions; moreover, hydrogen may be substituted for the alkali metal; besides, they are neutral and non-poisonous. On the contrary, in the unstable double cyanides hydrogen cannot be substituted for the alkali metal, and the heavy metal and even the cyanogen are more easily recognized by their reagents.

The necessity of expressing the special stability of one of the two classes of these compounds has caused them to be designated by special names: ferro-, ferri-, cobalto-, chromo-, chromi-, platino-cyanide, etc. Among the double cyanides, only the most important will be studied, and first among these the ferrocyanides and the ferri-cyanides.

## FERROCYANIDES.

FERROCYANIDE OF POTASSIUM,  $\text{Fe}(\text{CN})_6\text{K}_4$ —368.

Ferrocyanide of potassium has the following composition:

$$100\text{Fe}(\text{CN})_6\text{K}_4 = \begin{cases} \text{Fe} = 15.22 \\ \text{CN} = 42.39 \\ \text{K} = 42.39 \end{cases}$$


---


$$100.00$$

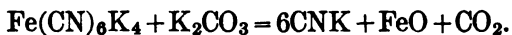
This salt, which is also called ferrocyanhydrate, cyanoferride, double cyanide of iron and of potassium, hydroferrocyanate, yellow prussiate of potash, corresponds to the formula  $\text{Fe}(\text{CN})_6\text{K}_4$ . It crystallizes with 3 molecules of water in voluminous monoclinic prisms. It has a citron-yellow color, is flexible, vitreous, and possesses a salty, bitter taste. Its density is 1.833. At  $60^\circ \text{C}$ . it loses its water of crystallization, which, however, does not completely disappear except at  $100^\circ \text{C}$ . It is then converted into a white powder. It is soluble in water, which dissolves two parts in cold and four in hot water. Its aqueous solution saturated at  $15^\circ \text{C}$ . has a density of 1.444.

In absence of air it fuses just below red heat with the production of nitrogen, potassium cyanide, and iron carbide:



In contact with air, potassium cyanate and peroxide of iron are formed.

When burned in the presence of an alkali it is entirely converted into cyanide of potassium:



These various reactions are of great importance and are utilized, as will be seen more in detail later, in the industrial manufacture of cyanides

Oxygen exerts no action on ferrocyanide of potassium, but ozone, the electric current, chlorine, bromine, dilute nitric acid, peroxide of lead, manganese dioxide, permanganate of potash, all transform it either wholly or in part into potassium ferricyanide. These various reactions may be expressed thus:

With chlorine,

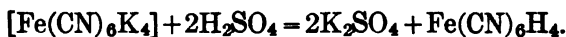


With the electric current,

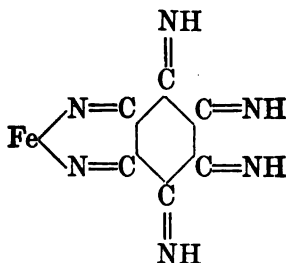


These two reactions are used industrially in the preparation of ferricyanide of potassium.

Sulphur converts it into sulphocyanate. When ferrocyanide of potassium is treated with dilute sulphuric acid there is formed hydroferrocyanic acid:



To hydroferrocyanic acid Friedel attributes the following formula:



With concentrated sulphuric acid there is formed carbon monoxide, sulphates of iron, potassium, and ammonium:



This reaction is explained as follows: The sulphuric acid is combined with iron and potassium sulphates; hydrocyanic acid in presence of moisture has yielded ammonium formate, which, acted upon by sulphuric acid, is converted into ammonia and carbon monoxide.

The ammonia thus formed unites with sulphuric acid to form sulphate of ammonia, while the carbon monoxide is set free.

The other alkali ferrocyanides of sodium and ammonium have similar properties. They are soluble in water, insoluble or only slightly soluble in alcohol.

Ferrocyanide of sodium,  $\text{Fe}(\text{CN})_6\text{Na}_4 + 12\text{H}_2\text{O}$ , has been proposed as a substitute for ferrocyanide of potassium, but so far it has not been possible to use it industrially on account of the enormous quantity of water of crystallization which it contains and which renders its transportation much more expensive.

The alkaline-earth ferrocyanides are white and insoluble.

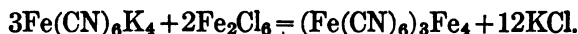
The other metallic ferrocyanides have various colors, which are frequently used in chemical analyses.

The most interesting are those of barium, which are white and very soluble; the cuprous salt, which is red, and the cupric, which is white; the nickel, which is greenish white, and the lead, which is white.

Ferrocyanide of iron is, among these latter, very interesting; the ferriferrocyanide is more generally known under the name Prussian blue:



This Prussian blue is formed by the action of a ferric salt on potassium ferrocyanide:



It is a dark-blue powder, odorless and insipid. Its fracture has a copper-like lustre. It loses its water of crystallization completely only when decomposed.

It is insoluble in water, alcohol, ether, and weak acids. It is soluble in ammonium tartrate and in oxalic acid, giving a violet solution in the former case and a blue solution in the latter.

When burned it yields carbonic acid, and water, and carbonate and cyanhydrate of ammonia.

When treated with concentrated sulphuric acid it is converted into a white pitchy mass, which on the addition of water is reconverted into Prussian blue. It is but slowly affected by hydrochloric acid. Potassium hydroxide converts it into ferric hydrate and potassium ferrocyanide. This reaction is utilized in the manufacture of potassium ferrocyanide extracted from the purifying materials of illuminating-gas.

The alkali carbonates act in the same way, but less easily.

Soluble Prussian blue is the name given to the compound formed by the union of ordinary Prussian blue with ferrocyanide of potassium.

#### FERRICYANIDES.

Beside the ferrocyanides is placed another class of double cyanides which is derived from them—the ferricyanides. Ferricyanides may be considered as double ferrocyanides minus 2 atoms of metal:



The tetratomic ferrocyanogen radical,  $\text{Fe}(\text{CN})_6$ , uniting with itself by exchanging two valences, is transformed into the hexatomic radical  $\text{Fe}_2(\text{CN})_{12}$ . Various authors consider the ferricyanides as double cyanides of ferric iron with another metal; others, on the other hand, think that they result from the union of a metal with the radical  $\text{Fe}_2(\text{CN})_{12}$ .

The following ferricyanides are known: Potassium, red; silver, orange; barium and potassium, black; calcium, gold color; cobalt, red; copper, yellow; nickel, greenish yellow.

The ferricyanides of the alkalis and of the alkaline earths only are soluble; the others are, as a rule, insoluble.

The most interesting is ferricyanide of potassium, also called cyaniferride, red prussiate of potash. The discovery of this salt was made by Gmelin. Its percentage composition is as follows:

$$100\text{Fe}_2(\text{CN})_{12}\text{K}_6 = \begin{cases} \text{Fe} = 17.02 \\ \text{CN} = 47.42 \\ \text{K} = 35.56 \end{cases}$$


---

100.00

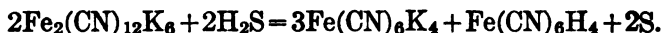
It occurs as red rhombic anhydrous prisms, having a density of 1.800 to 1.845 according to different investigators. It has a salty taste, is soluble in water, especially so in hot water. At 4.4° C. one part of the salt is soluble in 3.03 parts water, yielding a solution whose sp. gr. is 1.151. At 104° C. 1.22 parts water dissolve one part salt; the solution then has a density of 1.265.

Dilute solutions of ferrocyanide are orange-yellow; concentrated solutions are yellowish-brown. A solution of ferricyanide is decomposed in the light and on boiling, ferrocyanide being formed.

It is precipitated from its solutions of alcohol. Under the influence of heat it crackles, and is converted into ferrocyanide, nitrogen, cyanogen, Prussian blue, paracyanogen, and iron carbide.

When burned in the flame of a candle it emits sparks of iron.

Electrolysis and reducing agents, such as hydrogen sulphide, convert it into ferrocyanide:

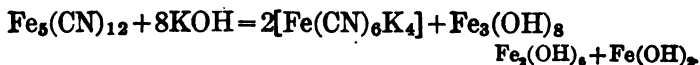


Nitric acid converts it into nitrate and nitroprusside of potassium. Red prussiate peroxidizes the greater part of metallic oxides.

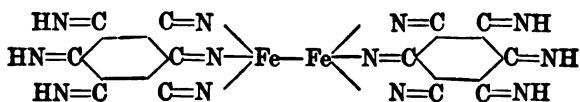
Hydrochloric acid decomposes a solution of ferricyanide of potassium, transforming it into ferricyanide of iron.

When treated with ammonia it yields ferrocyanide of potassium and of ammonium and nitrogen. It oxidizes phosphorus, sulphur, sulphurous acid, and sulphites; it converts oxalic acid and oxalates into carbonates. Organic substances in general, and especially in the presence of ferric salts, likewise exert a reducing action on ferricyanide of potassium. All these reactions are very easily carried out if one operates in alkaline solutions.

When a solution of a ferrous salt is treated with potassium ferricyanide a beautiful blue precipitate is obtained, which is called Turnbull's blue,  $\text{Fe}_5(\text{CN})_{12} + x\text{H}_2\text{O}$ . This blue is distinguished from Prussian blue in that when it is heated with carbonate or hydrate of potassium it yields ferroferric hydrate and yellow prussiate, while Prussian blue under the same conditions yields ferric hydrate:



Just as there is to the ferrocyanides a corresponding acid, hydroferrocyanic acid, so to the ferricyanides there is a corresponding acid, hydroferricyanic acid,  $\text{Fe}_2(\text{CN})_{12}\text{H}_6$ , which, according to Friedel, may be represented by the following formula:





Among the other interesting double cyanides must be mentioned the cobalticyanides, manganocyanides, and finally the platino- and platinicyanides.

#### COBALTICYANIDES.

Cobaltocobalticyanide is similar to Turnbull's blue. Hydrocobalticyanic acid is quite energetic, capable of decomposing carbonates, of dissolving iron and zinc, setting free hydrogen, and of neutralizing alkali bases. The most interesting of the cobalticyanides are those of potassium,  $\text{Co}_2(\text{CN})_{12}\text{K}_6$ , an anhydrous salt, pale yellow, slightly soluble in water, insoluble in alcohol; of copper,  $\text{Co}_2(\text{CN})_{12}\text{Cu}_3 + 7\text{H}_2\text{O}$ , clear blue, insoluble in water and in acids, soluble in ammonia. The cobalticyanide of nickel,  $\text{Co}_2(\text{CN})_{12}\text{Ni}_3 + 2\text{H}_2\text{O}$ , blue when moist, green when dry, insoluble in water and acids, soluble in ammonia.

The cobalticyanides are not toxic; they are in all respects analogous to ferricyanides.

#### MANGANOCYANIDES.

Manganocyanides are very unstable in air, which converts them into manganicyanides, which are likewise easily decomposable. Their solution is stable only in the presence of potassium cyanide.

#### PLATINOCYANIDES.

Platinocyanides correspond to the general formula  $\text{Pt}(\text{CN})_6\text{M}_2$ . They may be considered either as combinations of cyanide of platinum with a basic cyanide, or as the result of the union of a metal with the diatomic radical  $\text{Pt}(\text{CN})_6$ .

Soluble platinocyanides are obtained by dissolving platinocyanide in an alkali cyanide, or else by precipitating platinous chloride with potassium cyanide. The other platinocyanides are obtained by double decomposition.

Platinicyanides are obtained by the action of oxidizing agents on platinocyanides. Their mode of formation is doubtful; at present the best hypothesis known is that of Hadow, who considers the platinicyanides as a union of the platinocyanide with the oxidizing agent used in obtaining them.

## AUROCYANIDES.

More stress will be laid on the double cyanides of gold, or aurocyanides, on account of the impetus which they have given to the cyanide industry. Aurous cyanide unites easily with the cyanides of the other metals, yielding double cyanides, among which may be cited:

(1) Aurosoammonium cyanide,  $\text{Au}(\text{CN})_2\text{NH}_4$ , obtained by mixing saturated solutions of ammonium sulphite with auricopotassic cyanide. It is readily soluble in water and in alcohol. It is decomposed between  $200^\circ$  and  $250^\circ$  C.

(2) Aurosopotassic cyanide, or aurocyanide of potassium,  $\text{Au}(\text{CN})_2\text{K}$ , obtained by dissolving cyanide of gold, oxide of gold, or fulminating gold in potassium cyanide. It crystallizes in mother-of-pearl scales, is anhydrous, colorless, has a salty taste, is stable in air, soluble in 7 parts cold water, more soluble in boiling water, slightly soluble in alcohol, insoluble in ether. It is decomposed in a closed vessel, setting cyanogen free, and leaving a residue of potassium cyanide and gold. Acids break it up into aurous cyanide.

Auricopotassic cyanide, or auricyanide of potassium,  $\text{Au}(\text{CN})_4\text{K}$ , occurs as large colorless, efflorescent crystals capable of being fused into a liquid which sets cyanogen free and leaves behind metallic gold.

## NITROPRUSSIATES

Nitroprussiates, or nitroferricyanides, are obtained when nitric acid acts on the ferro- or ferricyanides. According to Gerhardt, the formation of these compounds is due rather to the action of nitrogen dioxide which is formed by the nitric acid.

This author ascribes to them the following formula:  $\text{Fe}(\text{CN})_5(\text{NO})\text{M}_2$  or  $\text{Fe}_2(\text{CN})_{10}(\text{NO})_2\text{M}_4$ . They are non-saturated ferrocyanides, of which the radical CN is replaced by NO, or may be considered as ferricyanides where  $2(\text{NO})$  replaces the group  $2(\text{CN})\text{M}$ .

These salts are generally highly colored. Those of potassium, sodium, ammonium, barium, calcium, and lead are dark red, readily soluble, and distinctly crystalline; those of copper, silver, zinc, iron, and nickel are insoluble. Alkalis decompose them, likewise does concentrated sulphuric acid; some of them dissolve Prussian blue. They give with sulphides purple color which is little stable. On heating them, nitrosulphides are produced.

## OXYGEN COMPOUNDS OF CYANOGEN.

CYANIC ACID,  $\text{CNOH} = 43$ .

$$100\text{CNOH} - \begin{cases} \text{C} - 27.90 \\ \text{N} - 32.56 \\ \text{O} - 37.21 \\ \text{H} - 2.33 \end{cases}$$


---


$$100.00$$

Cyanic acid is an oxygen compound of cyanogen, which was discovered in 1818 by Vauquelin, later studied by Woehler and Liebig.

Its formula is  $\text{CNOH}$ . It is monatomic. It is a colorless liquid, with sharp odor, the vapors of which irritate the eyes decidedly. It is soluble in water, but its solution readily breaks up into carbonic acid and ammonia. Its solution in ether is the only one which is stable. When its alcoholic solution is heated it yields esters of allophanic acid.

With metals it produces cyanates, salts which are quite stable when dry, except copper, mercury, and silver cyanates, but the presence of moisture breaks them up into carbonate and ammonia:



They are, as a rule, soluble. The cyanates of copper, mercury, and silver are only slightly soluble.

Dilute acids decompose them into cyanic acid, but quite often into carbonic acid and ammonia. With concentrated acids, cyanamide is formed.

The alkali cyanates are obtained by igniting in air the corresponding cyanides, especially in the presence of metallic oxides, as, e.g., oxide of lead, manganese, or copper.

CYANATE OF POTASSIUM,  $\text{CNOK} = 81$ .

$$100\text{CNOK} - \begin{cases} \text{C} - 14.81 \\ \text{N} - 17.29 \\ \text{O} - 19.76 \\ \text{K} - 48.14 \end{cases}$$


---


$$100.00$$

Cyanate of potassium occurs as transparent anhydrous crystals, soluble in water. It is obtained, generally, by heating manganese dioxide with potassium ferrocyanide to redness.

It is gradually decomposed by moist air and by water into carbonate of potassium and ammonium.

Potassium dissolves in melted cyanate, yielding cyanide and oxide. Cyanate of sodium,  $\text{CNONa}$ , has analogous properties.

Cyanate of ammonium is an isomer of urea, which it yields when heated at a moderate temperature,  $\text{CNOH} \cdot \text{NH}_3$ .

Silver cyanate is white, readily soluble in ammonia and dilute nitric acid. When heated it explodes rather violently, leaving a residue of silver carbide.

#### CYANURIC ACID AND TRICYANATES.

Cyanuric acid was discovered by Scheele and studied successively by Serullas, Woehler, and Liebig. It is obtained in many reactions, but the best method of producing it is that of Wurtz, which consists in passing dry chlorine through melted urea and treating the residue successively with cold and with boiling water. It is a solid, crystallizing in octahedrons, odorless, tasteless, readily soluble in water, alcohol, and concentrated mineral acids. It is acid in reaction. It volatilizes at  $360^\circ \text{C}$ ., when it is converted into cyanic acid. By prolonged boiling with concentrated acids it breaks up into carbonic acid and ammonia.

With metals it yields tricyanates, which are only slightly soluble. They are decomposed by strong acids which set cyanuric acid free. When the tricyanates are heated they are converted into cyanates.

#### SULPHOCYANIDES.

Sulphocyanides, or rhodanides as they are sometimes called, are really sulphocyanates. They are formed by the union of sulphocyanic acid with a metal. This sulphocyanic acid is really cyanic acid in which the oxygen has been replaced by sulphur:



For a long time it was wrongly considered as a hydrazid of the complex sulphocyanogen radical  $(\text{CN})\text{S}$ .

The sulphocyanides have the general formula  $(\text{CN})\text{SM}$ . Most of them are soluble in water, alcohol, and ether, especially those of the alkali metals. They easily form double salts. As to the

sulphocyanides of the heavy metals, they are insoluble, but are decomposed on boiling with the alkalis. Dilute acids decompose them even in the cold, with the exception of those of silver, mercury, and copper. In acid solution they are oxidized by permanganate of potash into hydrocyanic acid and sulphuric acid.

Among the many sulphocyanides only the most important will be studied.

**SULPHOCYANIDE OF POTASSIUM, CNSK = 97.**

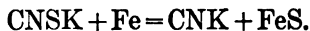
$$100(\text{CN})\text{SK} = \begin{cases} \text{C} = 12.37 \\ \text{N} = 14.44 \\ \text{S} = 32.99 \\ \text{K} = 40.20 \\ \hline 100.00 \end{cases}$$

This is an anhydrous, extremely deliquescent salt, crystallizing in prisms or in needles, of a density 1.886 to 1.906, very soluble in water and in alcohol (100 parts water dissolve 130 parts). Its solution in water is accompanied by an appreciable lowering of temperature (150 parts of this salt dissolved in 100 parts of water at 11° C. cause a temperature of -23° C.). It has a fresh and pungent taste, but it is not poisonous. According to physiologists, it occurs in the human saliva.

When ignited in air it is converted into potassium sulphate, though it is capable of withstanding a dull red heat for a long time without decomposition.

Its aqueous solution undergoes a slow decomposition, which may be hastened by application of heat. Ammonia is set free.

Chlorine and nitric acid decompose it. When heated with a metal, potassium cyanide and a metallic sulphide are formed:

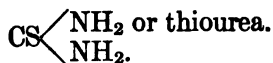


This reaction has been used as a means of obtaining the alkali-cyanides.

Sulphocyanide of sodium, (CN)SNa, has analogous properties.

Sulphocyanide of ammonium, (CN)SNH<sub>4</sub>, occurs in the form of deliquescent prisms readily soluble in alcohol and in water (105 parts in 100 water). A mixture of 133 parts of this salt with 100

parts of water at 13° C. causes a lowering of 31° in temperature. It melts at 159° C., and when heated to 170° C. it becomes transformed into sulphocarbamide:



When subjected to dry distillation it is decomposed, yielding hydrogen sulphide, and sulphides of carbon and ammonia, leaving a residue of *melam*. It is capable of dissolving salts of sulphur.

Silver sulphur cyanide is a white curdy precipitate, insoluble in water and ammonia, soluble in the sulphocyanides of ammonia and of potassium.

### ORGANIC COMPOUNDS.

By substitution of the group CN for OH hydrocyanic acid is capable with alcohols of forming hydrocyanic esters, which may be divided into two classes. In the first class, the alcoholic radical is attached to the carbon; in the second, it is attached to the nitrogen. These are isomeric bodies; the former are called nitriles and correspond to the general formula  $\text{R}-\text{C}\equiv\text{N}$ ; the latter are carbylamines or isonitriles, their formula being represented by  $\text{R}-\text{N}\equiv\text{C}$ . These are rather interesting bodies which should not be overlooked.

#### NITRILES AND CARBYLAMINES.

Nitriles are derived from amides through dehydration.

Nitriles possess general analogous properties whatever may be the atomicity of the alcohols from which they are derived; they form a clearly defined class of compounds.

Nitriles have the following properties

Under the influence of nascent hydrogen they fix 4 molecules of this element and form primary amines.

Under the influence of dehydrating agents nitriles fix 2 molecules of water and are converted into ammonia salts of acids containing the same number of carbon atoms as the hydrocyanic acid ester used. Thus methyl cyanide gives ammonium acetate.

They fix likewise one molecule of hydrogen sulphide in producing amido-sulphides. They unite with hydric acids, with negative chlorides, and with bromides.

The lowest member of the nitrile series is hydrocyanic acid, or formonitrile,  $\text{H}-\text{C}\equiv\text{N}$ . Among the most important may be cited:

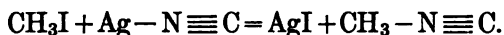
Methyl cyanide, or acetonitrile,  $\text{CH}_3\text{CN}$ , a colorless liquid, lighter than water (sp. gr. 0.81–0.83), volatilizing at  $77-78^\circ\text{C}$ ., having a pungent, aromatic, and ether-like odor. It is obtained by distilling ammonium acetate with anhydrous phosphoric acid.

Ethyl cyanide or propionitrile,  $\text{C}_2\text{H}_5\text{CN}$ , is a colorless liquid having an alliaceous odor, sp. gr. 0.78, boiling-point  $96.5^\circ\text{C}$ .

Propyl cyanide, or butyronitrile,  $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_2\text{CN}$ , having a density of 0.79 and boiling at  $116^\circ\text{C}$ .

Butyl cyanide,  $\text{C}_4\text{H}_9\text{CN}$ , density 0.816, boiling-point  $126^\circ\text{C}$ .; amyl cyanide,  $\text{C}_5\text{H}_{11}\text{CN}$ ; allyl cyanide,  $\text{CH}_2:\text{CH}\cdot\text{CH}_2\cdot\text{CN}$ , density 0.839, boiling-point  $118^\circ\text{C}$ .; cetyl cyanide,  $\text{C}_{16}\text{H}_{33}\text{CN}$ .

The properties of the hydrocyanic esters of the second class, or carbylamines, are quite different from those of the nitriles. They are generally formed by the action of alkyl iodides on silver cyanide:



Carbylamines are distinguished from nitriles, their isomers, by their odor, which is often disgusting, by their higher boiling-point, by their property of combining directly with acids, and finally by the action which hydrating and oxidizing agents produce upon them.

In this case they yield, as do the nitriles, two products, one fixed, the other variable, according to the ester employed. But here the fixed product is no longer ammonia, and the variable product an acid more or less rich in carbon. The first is always formic acid, while the latter is an ammonium compound. Thus methylcarbylamine, ethylcarbylamine, amylcarbylamine yield, respectively, with hydrating agents, by fixing 2 molecules of water, methylamine, ethylamine, and amylamine.

#### CYANIC ESTERS.

By its union with alcohol radicals, cyanic acid also yields cyanic esters, or alcoholic carbimides. The following only will be mentioned: Ethyl cyanate,  $\text{N} \begin{Bmatrix} \text{CO} \\ \text{C}_2\text{H}_5 \end{Bmatrix}$ , methyl cyanate, and butyl cyanate. These are mobile liquids, possessing repulsive odors and high boil-

ing-points. Potash converts them into primary amines. It is to Wurtz that we owe the discovery and study of these bodies. But these are not true cyanic esters.

The true cyanic esters were discovered by Cloez. They are isomeric with the esters discovered by Wurtz, but with this difference, that under the influence of hydrating agents they no longer yield amines and carbonic acid as do the carbimides, but behave themselves as ordinary esters and yield the same alcohol as was used at the start, and a cyanate or tricyanate. Their density is also somewhat higher.



## CHAPTER III.

### GENERAL PROPERTIES AND METHODS OF DETERMINATION OF THE VARIOUS CYANIDE COMPOUNDS.

#### I. ANALYTICAL PROPERTIES.

##### HYDROCYANIC ACID.

THE analytical properties hydrocyanic acid are the following:

*Silver nitrate*: White precipitate soluble in ammonia and in boiling nitric acid. Iron salts in the presence of alkalis: By adding potash and a few drops of a ferrous and a ferric salt to a hydrocyanic acid solution there is formed a precipitate. If this be treated with hydrochloric acid, the oxide of iron dissolves, and the liquid remains dark blue, due to the Prussian blue in suspension.

The following method can be used in the detection of even  $\frac{1}{2000}$ th part of hydrocyanic acid: To the liquid to be tested, add a little potash and a small amount of copper sulphate. This produces a precipitate of cyanide and hydrate of copper. By treating this precipitate with hydrochloric acid the hydrate dissolves, leaving a white residue of copper cyanide.

Liebig and Taylor's method is also quite delicate. This consists in converting hydrocyanic acid into ammonium sulphocyanate, by heating it with ammonium sulphide until decolorized. On adding a drop of a ferric salt to this sulphocyanate a blood-red coloration is produced.

##### CYANIDES.

*Silver nitrate* gives a white, curdy precipitate, soluble in excess of reagent, soluble in ammonium hydroxide, insoluble in dilute nitric acid. On igniting silver cyanide, it sets free cyanogen gas, burning with a purple flame.

*Ferrous-ferric salt* gives a dirty-green precipitate with neutral

solutions; a precipitate of Prussian blue and a ferrous-ferric oxide in alkaline solution. On addition of an acid the latter dissolves, leaving Prussian blue. Copper sulphide and tincture of guaiacum, if acidulated with a drop of hydrochloric acid, give an intense blue coloration.

*Acids* give free hydrocyanic acid, recognized by its odor of bitter almonds.

*Calcium chloride*: no precipitate.

*Ammonium sulphide* when heated with cyanides and evaporated to dryness, gives a red coloration on the addition of a ferric salt.

#### FERROCYANIDES.

*Calcium chloride* gives a precipitate in concentrated solutions. If the solution to be tested is only moderately concentrated, no precipitate occurs. Silver nitrate produces a reddish-brown precipitate insoluble in nitric acid and in ammonia.

*Ferrous sulphate* produces a white precipitate, which on exposure to the air rapidly changes to blue by oxidation. Chlorine and nitric acid oxidize this precipitate instantly.

*Ferric chloride* gives a precipitate of Prussian blue, insoluble in hydrochloric acid, but decomposed by boiling potash.

*Copper sulphate* gives a brownish-red precipitate insoluble in HCl.

*Concentrated sulphuric acid*, hot, sets free pure carbon monoxide. If the acid be dilute, hydrocyanic acid is set free.

#### FERRICYANIDES.

*Silver nitrate* gives an orange-yellow precipitate readily soluble in ammonia, insoluble in nitric acid.

*Calcium chloride*: no precipitate.

*Ferrous sulphate* produces a blue precipitate insoluble in HCl.

*Ferric chloride* yields brown coloration.

*Copper sulphate* gives greenish-yellow precipitate insoluble in HCl.

*Sulphuric acid* gives same reactions as with ferrocyanides.

#### SULPHOCYANIDES.

*Silver nitrate* gives a white flocculent precipitate, soluble in excess of the reagent, slightly soluble in ammonia.

*Calcium chloride*: no precipitate.

*Ferric chloride* produces a blood-red coloration, stable in the presence of  $\text{HCl}$ , but disappearing when exposed to heat or to the action of nitric acid, sulphurous acid, hyposulphites, or alkalis.

*Copper sulphate* and *sulphurous acid* give a white precipitate of copper sulphocyanide insoluble in acids, soluble in ammonia.

*Lead acetate* produces a crystalline precipitate which forms quite slowly.

*Sulphuric* or *hydrochloric acid* produces no effect if the sulphocyanide solution be dilute and cold; at the end of some time a yellow coloration takes place, and later a yellow precipitate of persulphocyanic acid; in warmth, carbon dioxide is set free, besides sulphide of carbon and hydrogen sulphide.

*Dilute nitric acid* gives, in warmth, a yellow deposit of persulphocyanogen.

*Molybdic acid dissolved in HCl* gives a red coloration which may be absorbed by ether.

#### CYANATES.

*Silver nitrate* produces a white precipitate which can be decomposed by heat and is soluble in ammonia and in nitric acid.

*Lead acetate* gives a white crystalline precipitate soluble in boiling water (distinct from that produced in hydrocyanic solution).

*Dilute and cold sulphuric acid* yields carbonic acid possessing a pungent odor due to a mixture of this acid with non-decomposed cyanic acid.

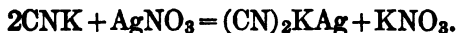
## II. METHODS FOR THE ANALYSES OF THE VARIOUS CYANIDE COMPOUNDS.

#### CYANIDES.

*Liebig's Method.*—This is a volumetric method based on the following reactions: If to a solution of potassium cyanide is added a solution of silver nitrate, there is formed silver cyanide soluble in the potassium cyanide still remaining in the solution. Cyanide of silver is formed permanently only when all the potassium cyanide has been converted into the double cyanide. The appearance of the slightest amount of a permanent precipitate indicates the end of the reaction:



or



One molecule or 170 grams of silver nitrate requires therefore two molecules or 130 grams of potassium cyanide to form one molecule of the double cyanide of silver and potassium. A solution of silver containing 13.056 grams of pure silver nitrate per liter is prepared, and another solution containing one gram of potassium cyanide in 100 cubic centimeters of distilled water is made, of which 10 cc. are used. Several drops of a solution of sodium chloride are added, and then the solution of silver nitrate is run in drop by drop until a permanent precipitation is formed. Each tenth of a cubic centimeter of the silver nitrate used corresponds to one milligram of potassium cyanide. Three or four titrations should be made and the average taken.

This method is applicable to solutions of hydrocyanic acid, which must first be saturated with potash:

If the cyanide contains chlorides, the method is not accurate. In this case the gravimetric method is preferable. The solution of cyanide is precipitated by silver nitrate, the precipitate is filtered, washed, dried, and weighed. Then it is boiled with HCl, which converts the silver cyanide into silver chloride. This is filtered, washed, dried, and weighed again. From the increase in weight may be calculated the quantity of cyanide. 1 gram CNK should give 2.058 grams CNAg.

*Fordos and Gelis' Method.*—This method is to be recommended. It is based on the ability of potassium cyanide to decolorize a solution of iodine in alcohol or in potassium iodide. The reaction is as follows:  $\text{CNK} + \text{I}_2 = \text{KI} + \text{CNI}$ . That is, there is a formation of potassium iodide and of cyanogen iodide, both of which are colorless. The end of the reaction is indicated by the yellow coloration of iodine in excess.

The iodine solution is prepared by dissolving 40 grams pure iodine in one liter alcohol of 33°. Five grams of the cyanide to be analyzed are dissolved in 500 cc. distilled water. 50 cc. of this

solution are transferred to a 2-liter flask, to which is added 1 liter of water and 100 cc. seltzer-water. The addition of this carbonated water converts the bases and carbonates to bicarbonates, which do not absorb iodine. Then the iodine solution is added drop by drop, stirring constantly, till the yellow coloration characteristic of iodine dissolved in potassium iodide appears.

From the volume of iodine solution used must be subtracted the quantity of cyanide, knowing that 254 parts of iodine are absorbed by 65 parts of potassium cyanide. If, at the end of the titration, the solution, colored by several drops of iodine in excess, has a turbid instead of a transparent appearance, this is an indication of the presence of alkaline sulphides. In this case it is best before titrating to remove the sulphides of the alkalis by means of a solution of lead acetate or of zinc sulphate, filtering and washing thoroughly.

The following table, calculated by Fordos and Gelis, gives the percentage of cyanide directly:

Iodine Absorbed.	Cyanide %.	Iodine Absorbed.	Cyanide %.	Iodine Absorbed.	Cyanide %.	Iodine Absorbed.	Cyanide %.
3.896	100	2.922	75	1.948	50	0.974	25
3.857	99	2.883	74	1.909	49	0.935	24
3.818	98	2.844	73	1.870	48	0.896	23
3.779	97	2.805	72	1.831	47	0.857	22
3.740	96	2.766	71	1.792	46	0.818	21
3.701	95	2.727	70	1.753	45	0.779	20
3.662	94	2.688	69	1.714	44	0.740	19
3.624	93	2.649	68	1.675	43	0.701	18
3.585	92	2.610	67	1.636	42	0.662	17
3.546	91	2.571	66	1.597	41	0.623	16
3.507	90	2.532	65	1.558	40	0.584	15
3.468	89	2.493	64	1.519	39	0.545	14
3.429	88	2.454	63	1.480	38	0.506	13
3.390	87	2.416	62	1.441	37	0.467	12
3.351	86	2.377	61	1.402	36	0.428	11
3.312	85	2.338	60	1.363	35	0.389	10
3.273	84	2.299	59	1.324	34	0.350	9
3.234	83	2.260	58	1.285	33	0.311	8
3.195	82	2.221	57	1.246	32	0.272	7
3.156	81	2.182	56	1.208	31	0.233	6
3.117	80	2.143	55	1.169	30	0.194	5
3.078	79	2.104	54	1.130	29	0.155	4
3.039	78	2.065	53	1.091	28	0.116	3
3.000	77	2.026	52	1.052	27	0.077	2
2.961	76	1.987	51	1.013	26	0.038	1

## ANALYSIS OF COMMERCIAL POTASSIUM CYANIDE.

There are numerous methods, but only the most interesting and the best adapted, either in manufacturing or in gold-mining, will be cited.

Commercial potassium cyanide quite often contains impurities, such as the carbonate, sulphate, cyanate, formate, sulphide, ferrocyanide, sulphocyanide, and sometimes chloride of potassium. *Carbonates* may be detected by dissolving the salt in water and adding acids, which will cause effervescence, or adding lime-water, which will produce a turbidity.

Cyanates may be detected in two ways:

(1) By extracting the salt with alcohol of 84° and adding concentrated hydrochloric acid to the alcoholic solution, when carbonic acid will be set free; or

(2) By adding ammonium chloride to the alcoholic solution and boiling urea is formed, which may be separated by evaporating to dryness on the water-bath, and taking up the residue with alcohol. When urea is acted upon by an alkaline hypobromite, nitrogen is set free.

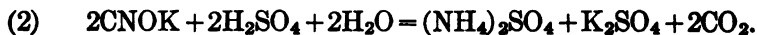
*Formates* may be detected by adding several drops of mercuric chloride to a boiling solution of cyanide, when, if formates are present, there will be produced a precipitate of calomel.

*Potassium sulphide* may be detected by the aid of lead salts, which give a black precipitate. If the cyanide contains ferrocyanide, its aqueous solution will give a precipitate of Prussian blue with a ferric salt (pure cyanide gives a greenish precipitate).

*Sulphocyanide* may be detected by treating the solution with a slight excess of HCl and then with ferric chloride, when a red coloration will be formed.

*Chlorides* may be detected by precipitating the solution with a slight excess of silver nitrate, and then boiling the precipitate in nitric acid. If the precipitate completely dissolves, there are no chlorides.

*Analysis of Cyanates.* (Method of O. Hertig, Zt. für angew. Chem. 1901, p. 619.)—The method is based on the decomposition of cyanates by hydrochloric or sulphuric acid, with formation of an ammoniacal salt:

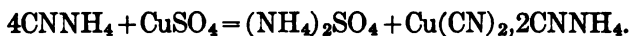


Dissolve 0.2–0.5 gram cyanide in a porcelain dish in several cubic centimeters of water. Add either dilute HCl or  $\text{H}_2\text{SO}_4$  and evaporate to dryness. Take up with water. The solution contains ammonia, which may be determined by boiling with soda, the ammonia being driven off and collected in  $n/5$  sulphuric acid, which is afterward titrated, using fluorescein as indicator.

*Determination of Potassium.*—If this is done by means of platinum chloride, after the cyanates have been decomposed with HCl, the presence of ammonium chloride may lead to errors. It is necessary in this case, after the cyanates have been decomposed by HCl, to drive off the ammonia at a dull red heat in a platinum dish.

**BUIGNET'S METHOD FOR THE DETERMINATION OF HYDROCYANIC ACID IN MEDICINE, AND IN DISTILLATES FROM BITTER ALMONDS OR LAUREL-CHERRY.**

This method is based on the fact that when a solution of hydrocyanic acid or an alkaline cyanide containing an excess of ammonia is treated with a solution of copper salt, there is first formed a double salt of copper and ammonium, which is colorless. When the reaction is complete, the ammonia acts on the copper salt added and gives the characteristic blue color. This indicates the end of the reaction, which takes place as follows:



For this purpose there is used a copper-sulphate solution containing 23.102 grams of the pure crystalline salt, free from efflorescence, per liter of water. Take 1 cc. of the medicinal hydrocyanic acid, or 100 cc. of the laurel-cherry or bitter-almond extract, or 0.5 gram of alkaline cyanide dissolved in about 100 cc. water, and to such a solution add 10 cc. ammonia, and stir. Then add, drop by drop, the solution of copper sulphate, stirring constantly, till the blue color becomes permanent. Each drop of the copper solution produces

at first a pinkish spot, which later changes to a delicate purple when the end reaction is near completion. At this point the further addition of copper salt must be done with care. This method is scarcely applicable except for cherry water-extract. It gives results which are inexact, especially if a too large amount of water be added, because the cuproammonium cyanide may be decomposed by water. It happens sometimes that even in the titration of the cherry solution there is formed, from the first, a permanent violet color, which interferes with the delicacy of the reaction, especially at the end. This may be remedied by the addition of carbonate of ammonia (10 cc. of a solution containing 1 part ammonium carbonate, 4 parts water, and 1 part strong ammonia).

#### FERROCYANIDES.

Erlenmeyer's method is the one most generally used in the determination of ferrocyanide. It is based on the precipitation of ferrocyanide as Prussian blue. It is both rapid and accurate.

Another method is based on the following: When an acidified solution of commercial ferrocyanide is treated with potassium permanganate, the potassium ferrocyanide alone produces an oxidation product capable of reproducing the raw material under the influence of ferrous oxide in alkaline solution, while none of the other oxidized substances are at all affected by this same ferrous oxide.

The mode of procedure is as follows: 3 grams of ferrocyanide are dissolved in water in a 500-cc. graduated flask. The solution is acidified with sulphuric acid, and then a concentrated solution of potassium permanganate is added until a permanent red coloration is obtained after several minutes' shaking. The solution is allowed to stand one-half hour. Caustic soda is then added in large excess, and the solution brought to the temperature of boiling water, with constant stirring. To the hot solution sulphate of iron is added till a black precipitate of magnetic iron oxide is produced. The solution is cooled, made up to 500 cc. with water, and filtered. In an aliquot of the filtrate, acidified with sulphuric acid, ferrocyanide is determined by titrating with potassium permanganate. This method requires about one hour.

There is another method, based on the insolubility of potassium



ferrocyanide in dilute alcohol, but it is applicable only when the solution contains at least 15% ferrocyanide.

To 70 cc. of 95° alcohol, acidified with acetic acid, 10 cc. of the ferrocyanide solution is added. The ferrocyanide is precipitated as a crystalline powder, which may easily be separated by filtration. After washing with 95° alcohol, the filter is dried at 100°, the precipitate redissolved in water and titrated with permanganate.

#### SULPHOCYANIDES.

The solution of sulphocyanide is precipitated with a standard solution of silver nitrate, using a ferric salt as indicator.

The blood-red color disappears as soon as there is an excess of silver solution showing the end of the reaction.

Or the reverse may be done, and this latter procedure is preferable: To a solution of sulphocyanide add an excess of standard silver nitrate, and titrate this excess with standard sulphocyanide. In this case the end of the reaction is indicated by the appearance of the permanent red coloration.

#### DETERMINATION OF FERROCYANIDES IN THE PURIFYING MATERIALS OF ILLUMINATING-GAS.

*Knublauch's Method.* (1889).—This method consists in transforming insoluble compounds into a soluble salt, purifying this product, and titrating the ferrocyanide therein by means of a copper salt.

250 grams substance are dried at 50–60° C. for 6 hours. The dried mass is passed through a sieve (360 meshes per sq. cm.). 10 grams of the sifted material are transferred to a graduated 255 cc. flask, and 50 cc. *n*/10 solution of potash added. Allow the solution to stand, with frequent shaking, for 15 hours. Fill the flask up to the 255-cc. mark and filter. 100 cc. of filtrate are added to an hydrochloric acid solution of ferric chloride (60 grams  $\text{FeCl}_3$  in 200 cc.  $\text{HCl}$  sp. gr. 1.19, and solution made up to a liter). The precipitate is rapidly filtered through a folded filter and washed with hot water. The filter and precipitate are transferred to a 250-cc. flask and treated with 20 cc. *n*/10 potash in order to convert the Prussian blue into ferrocyanide of potassium. The solu-

tion is then made up to 250 cc. and filtered. If filtrate contains no hydrogen sulphide, it is acidified and then titrated with a standard copper solution. If the filtrate contains hydrogen sulphide, it is advisable to add 1-2 grams lead carbonate, shaking, and filtering. 100 cc. of this filtrate (1.6 grams original material) are acidified with 5-6 cc.  $n/5$  sulphuric acid and then titrated with the following copper solution:

Water. . . . . 1000 cc.

Copper sulphate. . . . . 12-13 grams,

which is standardized by means of a solution of potassium ferrocyanide containing 4 grams of the pure salt per liter. The end of the reaction is noted by taking up a drop of the solution and moistening filter-paper which has been treated with ferric chloride.

*Moldenhader and Leybold's Method* (1889).—This consists in decomposing the ferrocyanides by evaporating them with sulphuric acid, and determining, by means of permanganate, the iron in the sulphate of iron remaining, after having previously converted it into the form of protoxide salt.

Place 50 grams of the finely pulverized substance in a liter flask with 100 cc. of an  $n/10$  solution of soda, containing also 2% anhydrous sodium carbonate. Let the flask stand in a warm place for 4 or 5 hours, then make up the solution to 1030 cc. Shake, filter, and evaporate 100 cc. of the filtrate in a porcelain dish to 10 cc. Transfer these 10 cc. to a platinum dish, add 25 cc.  $n/10$  solution of  $H_2SO_4$ , being careful of a too lively effervescence. Evaporate dry on a sand-bath, and heat the dish to redness. The residue in the dish is a mixture of ferric sulphate and bisulphate of sodium. Cool, and dissolve the mixture in  $n/10$  sulphuric acid, washing out the dish with this  $n/10$  sulphuric acid, so that about 100 cc. in all may be used, then rinse with 50 cc. hot water. Make up the solution to 250 cc., add 10 grams pure zinc and 1 cc.  $n/10$  copper sulphate solution. Heat on water-bath 3 hours; this reduces completely the ferric sulphate (test with potassium sulphocyanide). Cool, filter and dilute to 400 cc., and titrate with permanganate to a slight pink (deduct 0.4 cc., due to the same quantity of water, acid, copper, and zinc, in blank determination). From the number of cubic centimeters of permanganate used, the amount of ferrocyanide or of Prussian blue found in the spent oxide may be easily calculated.

*Burschell's Method.*—Treat 20 grams of the dried and pulverized mass, moistened with a little water, with 200 cc. of a solution of potassa (1-2). Shake and let stand several hours, then make up to 260 cc. (10 cc. extra due to the volume of the mass), shake and filter. Add 100 cc. of the filtrate to a solution of ferric alum dissolved in hot sulphuric acid. Filter the Berlin-blue precipitate, wash with hot water, and then transfer paper and precipitate to a 500-cc. flask. Add a little water, 15 grams mercuric oxide, and 1 gram ammonium sulphate. Heat to boiling for about a quarter of an hour, and after cooling add 1 cc. of a saturated solution of mercurous nitrate,  $\text{Hg}_2(\text{NO}_3)_2$ , and ammonia so long as a precipitate is formed. Make a solution up to 500 cc., shake and filter. Transfer 200 cc. of the filtrate to a 400-cc. flask, add 6 cc. ammonia (sp. gr. 0.9) and 7 grams zinc powder (the cyanogen in cyanide of mercury is thus transposed, and recombined as ammonium cyanide), shake for a few minutes, then add 2 cc. of a 30% solution of potassia and make up to 400 cc. Shake and filter.

Allow 100 cc. of the filtrate (=0.875 gram original substance) to run into an excess of  $n/10$  solution silver nitrate (40 cc. are generally enough) contained in a 400-cc. flask. Add dilute nitric acid and make up to 400 cc. Filter and titrate 200 cc. of the filtrate with an  $n/20$  solution of ammonium sulphocyanide after first adding 5 cc. of a saturated solution of iron alum.

The end of the reaction is indicated by a clear brown coloration. 1 cc.  $n/10$  silver-nitrate solution corresponds to 0.007042 gram:  $\text{Fe}(\text{CN})_6\text{K}_4 + 3\text{H}_2\text{O}$  or to 0.003832 gram Prussian blue.

*Zaloziecki's Method* (Zt. für angew. Chem. 1890, p. 210).—20 grams of the dry, pulverized purifying material are transferred to a 100-cc. cylinder with 20 cc. of a 10% solution of potassa. Heat on water-bath one half-hour, cool, make up to 100 cc.; take 45 cc., which corresponds to 10 grams original substance (assuming that the 20 grams occupy a volume equal to 10 cc.), and heat over free flame till no more ammonia is set free. Neutralize the solution exactly with dilute HCl or  $\text{H}_2\text{SO}_4$ , using phenolphthalein as indicator. When the solution is neutralized, add 20 cc. normal potassium carbonate and 5 grams moist zinc carbonate, heat one half-hour while passing a stream of carbonic acid through the solution.

After cooling, dilute to 100 cc., and titrate 50 cc. (=5 grams substance) with  $n/10$  acid, using methyl orange as indicator.

By deducting the amount of acid equivalent to 10 cc. potassium carbonate normal solution and multiplying the remaining number of cubic centimeters by 0.46, the per cent of potassium ferrocyanide,  $\text{Fe}(\text{CN})_6\text{K}_4 + 3\text{H}_2\text{O}$ , is obtained.

*E. Donath and B. M. Margosche's Method* (Zt. für angew. Chem. 1899, p. 345).—This method is based on the fact that the ferrocyanides and ferricyanides of the alkalis are easily decomposed, in alkaline solution, by oxidizing agents.

The whole of iron separates as ferric oxide, and this element may be quite accurately determined in the precipitate, by known methods. The following is the mode of procedure:

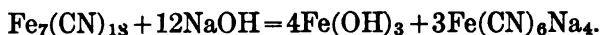
Grind the purifying material quickly in an iron mortar. Transfer 50 grams into a liter flask, add 100–150 cc. of a 15% solution of caustic potash. Allow the flask to stand in a warm place for some time, shaking frequently. Complete the volume to 1030 cc. and filter through a folded filter. To an aliquot part of the filtrate add a bromated solution of caustic soda (prepared by dissolving 80 grams of sodium hydrate in water, cooling and making up to 1000 cc., and adding 20 cc. of bromine, shaking thoroughly). Heat for some time. Under these conditions there is formed an abundant, thick, pulverulent precipitate of a beautiful brick-red color, together with a lively liberation of gas. Let the precipitate settle several hours, filter and wash. It may be dissolved on the paper with hot dilute HCl and the iron reprecipitated with ammonia. But it is preferable to dry the precipitate on the paper, then to transfer it to a small flask, to burn the paper, and fuse the ash thus obtained with potassium bisulphate, and to add this product to the remainder of the precipitate in the flask. The whole is then dissolved in dilute sulphuric acid. Reduce with zinc and titrate the iron by means of potassium permanganate.

The amount of iron multiplied by 7.5476 gives the quantity of crystallized salt,  $\text{K}_4\text{Fe}(\text{CN})_6 + 3\text{H}_2\text{O}$ , or multiplied by 6.5833 gives the amount of anhydrous salt.

## DETERMINATION OF PRUSSIAN BLUE IN THE SPENT OXIDES.

Method of Dr. Nauss of the gas-works at Carlsruhe.

This is based on the decomposition of Prussian blue by alkalis, which are combined as follows:



Prussian blue is treated with hot caustic soda, the reaction being complete when the green coloration has disappeared.

The following is the mode of procedure:

Weigh 10 grams of the material and place in a 500-cc. flask containing 50 cc. of a 10% solution of caustic soda. Shake often, and allow the flask to stand at ordinary temperature till the whole of the blue has been decomposed by the caustic alkali. This requires about 15 hours. The formation of sodium sulphide is avoided if a dilute solution of soda be used. When the decomposition is ended make solution up to 505 cc. with water (the 5 cc. extra are for the volume of iron oxide). Shake thoroughly and filter. Take an aliquot part—e.g. 50 cc. = 1 gram substance—add 10–15 cc. of a hot acid solution (consisting of 200 grams ferric alum, one liter water, and 100 cc. sulphuric acid) in order to decompose the sodium ferrocyanide contained in the Prussian blue. Heat on water-bath till the pungent odor is no longer apparent and filter through a funnel surrounded with hot water. Wash with hot water till the filtrate is free from sulphuric acid. The residue which contains all the Prussian blue is transferred to a flask to which water is added. Bring the solution to boiling, stirring continually. The quantity of blue may then be determined with a solution of sodium hydroxide. It is necessary in order to decompose the whole of the blue to add successively the required amount of  $n/50$  solution. The decomposition takes place rapidly if the solution be heated several moments, and the excess of the sodium hydroxide may be titrated anew against  $n/50$  acid. The reaction is ended when the green coloration is permanent.

## TOXICOLOGICAL RESEARCH.

Substances in which the existence of cyanogen compounds is suspected are finely divided and diluted with distilled water so as to form a light pulpy mass. This is acidified with tartaric or

phosphoric acid (acids which have no action on hydrocyanic acid, but capable of setting it free from cyanides). This mixture is placed in a tubular retort provided with a straight safety-tube and connected with a bent tube which plunges to the bottom of a double tubular Woolf bottle. This latter is connected with a bulb-tube. Both of these contain a dilute solution of silver nitrate. Heat gently on the water-bath so as to produce a slow ebullition, which must be carefully watched. Under these conditions the presence of hydrocyanic acid is shown by the formation of a white precipitate of silver cyanide in the Woolf bottle and in the bulb-tube. When the precipitate no longer increases the distillation is stopped. Cool and unite the solutions of the bulb-tube and the bottle; filter, wash, dry at  $100^{\circ}$  C., and weigh.

But as quite often substances to be analyzed contain hydrochloric acid, which would give a perfectly analogous precipitate, it is well to make sure, by means of the ordinary reactions which we have already described, that one has really to do with cyanogen or its compounds.

Moreover, it is to be noted that cyanide of mercury gives neither the reactions of mercury nor those of the cyanides. One may either precipitate the mercury with hydrogen sulphide, filter, and test for hydrocyanic acid, as indicated above, or else, and this is preferable, plunge blades of iron for a sufficient length of time into the extracted solutions of the substances suspected, which have been acidified with sulphuric acid. The mercury is precipitated by the hydrogen and the cyanogen converted into hydrocyanic acid.

## CHAPTER IV.

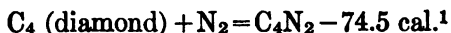
### THERMOCHEMICAL DATA RELATING TO THE CYANIDE COMPOUNDS.

IN order to complete this general study it seems necessary to give some thermochemical information relative to the principal cyanated compounds.

The following outline is taken from Berthelot's remarkable work *Sur la force des matières explosives, d'après la thermo-chémie* (t. II., p. 64, etc.):

#### I. CYANOGEN.

The heat of formation of cyanogen determined by Berthelot by ordinary combustion or by detonation is



From this number Berthelot draws the following conclusions:

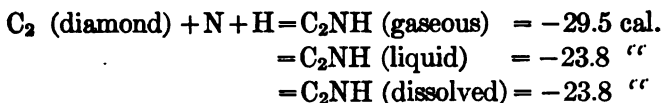
"Cyanogen ( $\text{C}_2\text{N}$ ), as well as acetylene ( $\text{C}_2\text{H}$ ) and nitrogen dioxide ( $\text{NO}_2$ ) and all substances which play the rôle of true compound radicals, is a body whose formation is accompanied by the absorption of heat, a circumstance which seems to be of such a nature as to explain the very character of this real compound radical, manifesting in its combinations a greater energy than in its free elements. The energy of these latter becomes stronger rather than weaker because of this absorption of heat, as is the case in combinations which give off heat, and this increase of energy renders the compound system comparable to the most active elements."

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<sup>1</sup> The same notation is used in this chapter as that used in Berthelot's work.

## II. HYDROCYANIC ACID.

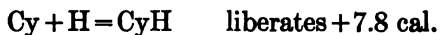
The heat of formation of hydrocyanic acid, determined by various methods by Berthelot, may be expressed thus:



"It follows from these figures," says Berthelot, "that hydrocyanic acid is formed from its elements with absorption of heat, which explains the readiness with which this acid forms direct combinations, polymeric compounds, and brings about complex reactions."

Berthelot remarks further that "cyanogen and hydrocyanic acid, acetylene, etc., could be regarded as formed with liberation of heat, if it were admitted that carbon, when considered as diamond or charcoal, does not correspond to the real elementary carbon, which should be comparable to hydrogen and probably gaseous, while the diamond and charcoal represent its allotropic modifications. In passing from its gaseous to its polymeric and condensed state, elementary carbon would liberate a considerable quantity of heat, and greater than the heat absorbed in the formations of acetylene ( $-30.5$  cal. for  $\text{C}_2=12$ ), and of cyanogen ( $-37.3$  cal.)"

The actual figures show that the formation of hydrocyanic gas starting with cyanogen and hydrogen is



"This formation is therefore exothermic," a circumstance which led Berthelot to foresee that it could be brought about directly; and, in fact, the illustrious savant did succeed, contrary to the negative experiments previously worked out by Gay-Lussac, in combining the two gases directly under the influence only of time and heat. The synthesis of hydrocyanic acid by means of acetylene and nitrogen, both in the free state, by the electric spark, which was discovered by Berthelot in 1868, liberates  $+2.1$  cal.



## III. CYANIDE OF POTASSIUM.

The heat liberated by the formation, from its elements, of solid cyanide of potassium, determined by Berthelot, is as follows:



The direct formation of potassium cyanide, by means of the union of its elements, in the same proportion by weight as represented by the equation, cannot be brought about, in fact, at the ordinary temperature. But it is admitted that it does take place at a very high temperature, if free nitrogen is made to act upon charcoal impregnated with potassium carbonate, that is, under the conditions where nascent potassium is formed.

"At this temperature cyanide of potassium is a liquid, perhaps even gaseous, change of state which absorbs heat, but on the other hand the potassium is gaseous, which fact somewhat compensates. If the free nitrogen, carbon, and potassium really do combine, without other intermediary reaction, as, e.g., the formation of an acetylide (which has not been proved), one will have to admit that the total synthesis of cyanide of potassium liberates heat under the real conditions in which it is effected.

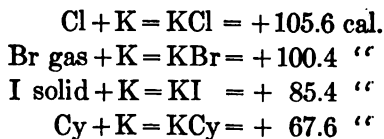
"Whether the liberation is produced all at once or only by successive reactions, it explains the total synthesis no less.

"The union of cyanogen with potassium takes place, as is known directly. This union calculated for the following states:



"This figure justifies the direct synthesis of cyanide of potassium by means of cyanogen, but the heat liberated is less than that liberated in the union of the same metal with the gaseous halogen elements."

The latter is



Berthelot attributes to this inferiority in the amount of heat liberated the decomposition of solutions of potassium cyanide by

the halogens, and further says that "the cyanogen which should be set free is combined moreover with one half of the halogen body, not without a slight liberation of additional heat (+1.6 cal. for CyCl gas, +4.2 cal. for CyI solid). Then he compares the quantities of heat liberated when starting with the hydracids and dilute base:



which is a quantity much less than that liberated in the formation of the chloride, bromide, or iodide of potassium (+13.7 cal.). With gaseous hydracids the disagreement is still greater (+17 cal.). Berthelot concludes from this that "hydrocyanic acid is a much weaker acid than the hydracids derived from the halogen elements, and that it is even displaced in potassium cyanide dissolved by most of the acids.

"The transformation of potassium cyanide into potassium formate:



"That is the reaction which goes on slowly in solutions of potassium cyanide.

"The same reaction carried on on the dry salt by water-vapor produces formate, and also ammonia gas. It is much more rapid, but it also liberates twice the amount of heat, +17.7 cal. If the temperature is raised, this reaction becomes complicated because of the subsequent destruction of the formate by heat or by an excess of alkali, a reaction which takes place at about 300° and which transforms completely potassium cyanide into potassium carbonate:

$$\text{C}_2\text{NK solid} + \text{KO} \cdot \text{OH solid} + 2\text{H}_2\text{O}_2 \text{ gaseous} \\ = \text{C}_2\text{O}_4 + 2\text{KO solid} + \text{NH}_3 \text{ gas liberates } +37.4 \text{ cal.}$$

"I call attention to this because it is one of the most active causes of the destruction of potassium cyanide during its manufacture, where one works with the fused salts, a fact which slightly modifies the figures above, without modifying the general significance of them."

## IV. CYANHYDRATE OF AMMONIA.

The formation of solid ammonium cyanide starting with gaseous hydrocyanic acid and gaseous ammonia liberates +20.5 cal., and starting with the elements +40.5 cal.

## V. FERROCYANIDE OF POTASSIUM.

Because of the difficulty in obtaining pure hydroferrocyanic acid Berthelot determined the heat of formation of this acid in an indirect way, i.e., by displacing it from its salts by a more energetic acid.

" By mixing a dilute solution of potassium ferrocyanide,  $\text{Cy}_3\text{FeK}_2$  = 4 liters, with dilute hydrochloric acid (1 equiv. = 2 liters), no change of temperature is observed; either there is no reaction, or the two acids liberate the same quantity of heat in combining with the potassa, in which case the base in the solution could be divided. The latter case is the more likely. In fact, by mixing ferrocyanide with dilute sulphuric acid a progressive separation and a displacement which tends to become complete, in the presence of a large excess of sulphuric acid, are observed. Thus

$\text{Cy}_3\text{FeK}_2$  (6 liters) +  $\text{HSO}_4$  (1 equiv. = 2 liters) liberates +1.107 cal.

$\text{Cy}_3\text{FeK}_2$  (6 liters) +  $2\text{HSO}_4$  (1 equiv. = 2 liters) liberates +0.181 cal.

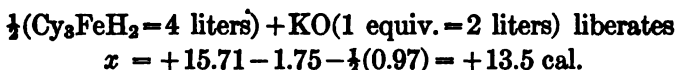
By continuing the gradual addition of sulphuric acid an absorption of heat is produced, due to the formation of bisulphate.

" With a large excess added all at one time

$\text{Cy}_3\text{FeK}_2$  (4 liters) +  $10\text{HSO}_4$  (1 equiv. = 2 liters) liberates +0.966 cal.

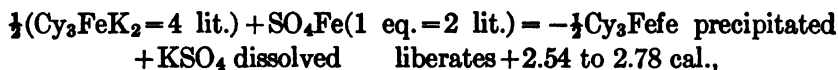
" These phenomena are comparable to the reaction of sulphuric acid on the chlorides, although the results are somewhat different. Here likewise is a progressive division of the base between the two acids. If it be admitted that the  $10\text{HSO}_4$  be sufficient to remove almost the whole of the potassa from the ferrocyanide, similar to that which is produced with the chlorides, nitrates, etc., the heat  $x$  liberated in the reaction of dissolved hydroferrocyanic acid on

dilute potassa may be calculated. In fact, +15.7 cal. being the heat liberated in the reaction of sulphuric acid on potassa, and -1.75 cal. the heat absorbed in the reaction of dilute  $4\text{HSO}_4$  on dissolved potassium sulphate (formation of bisulphate), the desired reaction will be

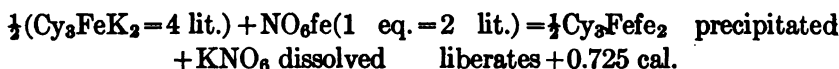


" This figure is practically the same as that which represents the heat liberated by hydrochloric acid and nitric acid when acting on potassa, from which it follows that hydroferrocyanic acid is a strong acid comparable to the mineral acids. It is known that it displaces carbonic and acetic acids. The absence of apparent thermic reaction between  $\text{HCl}$  and dissolved cyanoferride is in harmony with these results.

" Nothing is easier than passing through that to the formation of Prussian blue; in fact

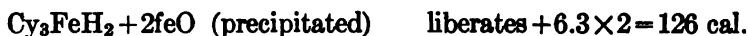


the amount of heat liberated increasing with length of time, as often happens in the formation of amorphous precipitates. Likewise



" From the results obtained with ferric sulphate, the substitution of potassa for iron peroxide ( $\text{KO}$  for  $\text{FeO}$ ) in Prussian blue liberates +7.2 cal.; from the results obtained with the nitrate, +7.2 cal., a perfect agreement.

" By admitting that the formation of cyanoferride of potassium,  $\text{CyFeH}_2$  (dilute) +  $2\text{KO}$  dilute, liberates  $+13.5 \times 2 = 27.0$  cal., it is thereby concluded that the formation of Prussian blue with the same acid and precipitated peroxide of iron,



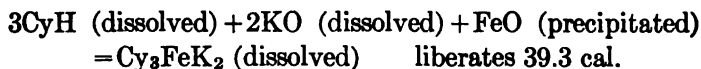
"The value 6.3 differs but little from 5.7, which represents the union of nitric and hydrochloric acids with iron peroxide, which fact is a new proof of the analogy between hydroferrocyanic acid and the mineral acids. Nevertheless +6.3 is greater than +5.7, which fact explains why dilute hydrochloric acid does not decompose Prussian blue with formation of iron chloride.

"Hydrocyanic acid, one of the weakest acids known, has formed therefore, by its association with iron cyanide, a powerful acid, comparable in all points to hydrochloric and nitric acids.

"This is a new proof calculated to establish the fact that the best characterized acid properties, even in the hydrocarbon compounds, are not necessarily connected with the presence of oxygen.

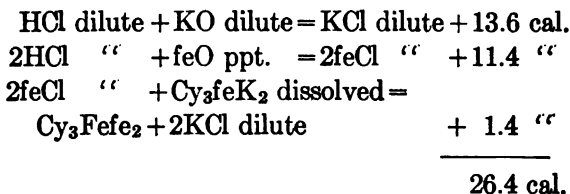
"The heat liberated in the formation of cyanoferride itself remains to be determined.

"I found the following results:  $\text{SO}_4\text{Fe}$  (1 eq.=2 lit.) +  $2\text{SO}_4\text{Fe}$  (1 eq.=2 lit.) +  $6\text{KO}$  (1 eq.=2 lit.) liberates 23.2 cal. By adding to the above mixture  $3\text{CyH}$  (1 eq.=4 lit.) a further liberation of +39.3 cal. is observed, which represents the formation of cyanoferride, starting with  $\text{CNH}$  and the two oxides:



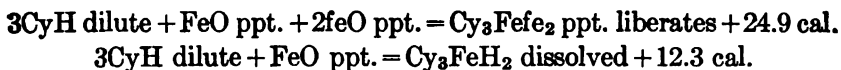
"As a control experiment, I added to the solution  $3\text{HCl}$  (1 eq.=2 lit.), which liberated +25.0 cal., with the formation of an abundant precipitate of Prussian blue, the heat liberated varying during the precipitation from 23.0 to 25.0 cal.

"In short,  $\text{HCl}$  has produced the following reactions:

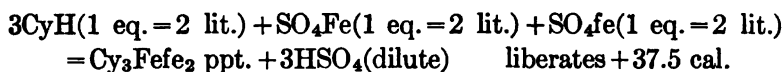


"The agreement between 25.0 and 26.4 is as close as one may expect when working with similar precipitates, the state of which varies with the conditions.

" From that I conclude



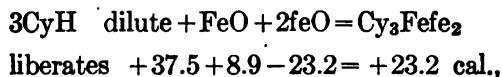
" I verified these values by forming Prussian blue directly by means of CNH and the two sulphates:



" The difference between the heat of formation of alkali sulphate and that of iron sulphate starting from the oxides being

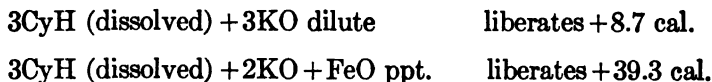
$$12.5 + 11.1 - 47.1 = -23.5 \text{ cal.,}$$

and the heat of formation of 3CyK starting from potassa being +8.9 cal., from these data the heat liberated in the formation of Prussian blue from CNH is easily found:



a result which shows sufficient agreement with +24.9 cal., obtained in another way, but which I regard as a little less exact.

" Let us draw some general conclusions from these results. The first conclusion is in regard to the heat liberated in the formation of cyanoferride, starting with hydrocyanic acid or with potassium cyanide:



" The substitution of ferrous oxide for potassa with formation of cyanoferride liberates a large amount of heat, i.e., +39.3 - 8.7 = +30.6 cal. One single equivalent of ferrous oxide contributes, moreover, to the formation of hydroferrocyanic acid.

" This figure explains, besides, the observed displacement, and it corresponds to the constitution of a new molecular type, that of hydroferrocyanic acid.

" In fact, we conclude from that

$3\text{CyH}$  (dissolved) +  $\text{FeO}$  ppt. liberates +12.3 cal., a quantity greater than the heat (+9.0 cal.) liberated by  $3\text{KO}$  (dilute) united with  $3\text{CyH}$ .

" That is because here there are two simultaneous reactions: the union of 3 mol. of  $\text{CNH}$  into a type thrice as much condensed, and the combination of ferrous oxide which enters the constitution of this new type  $\text{Cy}_3\text{FeH}_2$ .

" Likewise, in the case of Prussian blue, it has elsewhere been established that  $\text{Cy}_3\text{FeH}_2$  (dilute) +  $2\text{FeO}$  ppt. liberates +12.6 cal. =  $6.3 \times 2$ , i.e., practically the same number as the union of the same oxide with dilute  $\text{HCl}$  and  $\text{HNO}_3$ .

" Starting from  $\text{CNH}$  itself we have



" The magnitude of this last figure, which is three times the heat liberated when potassa unites with hydrocyanic acid, is the explanation, as above, of the formation of the new molecular type of cyanoferrides, and still more so of the formation of the double cyanides.

" This superposition of effects explains, moreover, the superiority of apparent affinities which the oxide of iron shows over potassa in its union with hydrocyanic acid, which is shown by a greater liberation of heat than in the formation of ordinary oxysalts, sulphates, nitrates, acetates, etc., starting with the dilute acids and alkaline bases corresponding to the metallic oxides.

" Would it not be possible to find some analogous circumstance to explain how the oxides of silver and of mercury, besides the oxides of iron, liberate more heat than does dilute potassa in uniting with hydrocyanic acid? That is, are the cyanides of silver and of mercury really represented by the simple formulas  $\text{CyAg}$ ,  $\text{CyHg}$ , salts comparable to those of  $\text{CyK}$  and  $\text{CyH}$ , or else would it not be better to regard them as a more condensed type of cyanides, such as

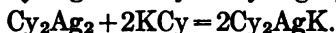


" The heat liberated by their union with cyanide of potassium

in the formation of double cyanides, even in the state of dilute solutions, such as



would support this supposition, for it would be the result of the passage from the simple type, cyanide of potassium, to the complex type which constitutes the double cyanides,

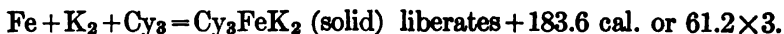


" Besides, hydrocyanic acid is not the only acid which is the occasion of a general overthrowing of the ordinary affinities, interpreted by the corresponding thermic effects between the alkaline oxides and the metallic oxides. Hydrogen sulphide is in exactly the same case.

" Notwithstanding these latter considerations it remains no less a fact that the metallic oxides liberate more heat than the alkaline bases, uniting with hydrocyanic acid, a fact which explains why they displace them. Thermochemistry thus takes into account the constitution of the complex cyanides, new molecular types, which are very superior to the primitive type because of the energy of their affinities in regard to the bases, as well as because of the stability of the resultant salts—I mean very superior to hydrocyanic acid, which contributes to their formation by condensation.

" Hydrocyanic acid, common generant of condensed types, is distinguished, moreover, because it is formed from the elements with an absorption of heat—29.5 cal.; in other words, its formation has stored up an excess of energy which makes it specially fit for successive combinations and molecular condensations.

" Let us give, finally, the heat of formation of potassium ferro-cyanide from its elements:



From simple bodies:



These results are close to those which are obtained in the formation of potassium cyanide, starting with cyanogen +67.6 cal., and with the elements +30.3 cal.



"The hydrated salt encloses 3 molecules of  $\text{H}_2\text{O}(3\text{HO})$ , extra, whose union in the liquid form with the anhydrous salt liberated +2.48 cal., which brings the total amount of heat liberated in the formation of the crystalline yellow prussiate from the elements and  $\text{H}_2\text{O}$ , +94.2 cal."

#### VI. POTASSIUM CYANATE.

The formation of solid potassium cyanate from the elements is  
 $\text{C}_2 \text{ diamond} + \text{N} + \text{K} + \text{O}_2 = \text{C}_2\text{NKO}_2$  liberates +102.0 cal.

The dissolved salt liberates +96.8 cal.

The same formation starting with dilute KOH:

$\text{C}_2 + \text{N} + \text{OKO dilute} = \text{C}_2\text{NKO}_2$  (dissolved) liberates +15.5 cal.

From gaseous Cy:

$\text{Cy} + \text{K} + \text{O}_2 = \text{CyKO}_2$  solid +139.3 cal.

$\text{Cy} + \text{O} + \text{KO dilute} = \text{CyKO}_2$  dissolved + 51.8 "

$\text{Cy}_2 + 2\text{KO dilute} = \text{CyKO}_4 \text{ dilute} + \text{CyK dilute} + 34.2 "$

All these results are greater than the heat liberated in the analogous reactions of the real halogen elements, e.g.,

$\text{Cl}_2 \text{ gas} + 2\text{KO dilute} = \text{ClO}_2\text{K} + \text{KCl dissolved}$  liberates only +25.4 cal.

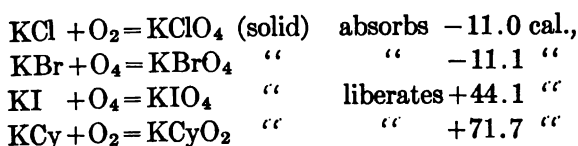
There is, moreover, this difference, that the complex nature of Cy and its tendency either to form polymeric and other condensed bodies, or to regenerate ammonia and its derivatives, are the cause of a number of secondary reactions, such as do not occur in the case of chlorine. These reactions are easier in proportion as the heat liberated by the direct reaction is greater and in proportion as it furnishes from that time a greater reserve of energy by other transformations.

"The union of dry potassium cyanide with gaseous oxygen in the formation of solid cyanate  $\text{C}_2\text{NK (solid)} + \text{O}_2 \text{ (gas)} = \text{C}_2\text{NO}_2\text{K (solid)}$  would liberate +102.0 - 30.3 = +71.7 cal., a large figure, and about three fourths of the heat (+94.0) liberated by the combustion of the carbon contained in the cyanide.

"This figure refers to bodies taken in their actual state, a fact in which, up till now, no absorption of oxygen by the cyanide of

potassium has been observed, probably because it has not been investigated. In the fused state, on the other hand, it easily takes place, as is known. Now these figures just calculated may be approximately applied to the same bodies, under the known conditions of their real reaction, at a high temperature, for the fusion of the cyanide as well as of the cyanate should absorb about equal quantities of heat.

" Considering the heat liberated by the oxidation of its potassium compound, cyanogen agrees more with iodine, and differs, on the contrary, with chlorine. We have in fact:

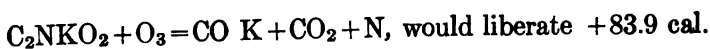


a progression inverse to that which characterizes the union of a like metal, such as K, with the same series of halogen bodies, such as Cl (+105.0 cal.), gaseous Br (+100.4 cal.), gaseous I (+85.4 cal.), and cyanogen (+67.6 cal.)

" From the preceding figures is explained why cyanide of potassium has such a great tendency to oxidation, either under the influence of oxidizing agents, or even in air.

"The combustible character of one of the elements of cyanogen opposes, moreover, the formation of peroxidized acids, as with chlorine, and the halogen elements such compounds would have too great a tendency to being converted into carbonic acid.

" The complete combustion of solid potassium cyanate,



"The facility with which potassium cyanate becomes regenerated from ammonia, even from the one fact of its long contact with water, is easily explained:

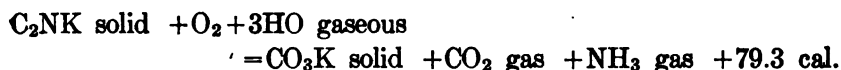


"That is also an amide reaction.

"The well-known transformation of fused cyanate of potassium

by means of water-vapor into fused carbonate of potassium, carbonic acid, and ammonia liberates about +9 cal.

"The conversion of potassium cyanide into carbonate and ammonia under the combined influence of oxygen and water-vapor at a high temperature, a conversion so pernicious in the industrial preparation of prussiates, is no less easily explained by thermochemistry. In fact, at the ordinary temperature we should have



At about red heat this figure should remain likewise large, the cyanide and the carbonate being partially fused."

For the thermochemical data referring to cyanogen and its compounds see the tables at end of the book.

## PART TWO.

### THE PRESENT CONDITION OF THE CYANIDE INDUSTRY.

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#### CHAPTER V.

#### COMMERCIAL AND INDUSTRIAL STUDY.

THE development of the industry of the cyanated compounds is due, as was stated in the Introduction, primarily to the use of potassium cyanide in the treatment of auriferous minerals.

At first the production of cyanides was, so to speak, insignificant, or at least limited. The industry was created in 1710 with the discovery of Prussian blue, by the dyer Diesbach, and for a long time was limited to this compound used in dyeing. The discovery of potassium ferrocyanide and the other cyanogen compounds came, but later, and among these the ferrocyanide alone was applied in the arts and manufactures. Cyanide of potassium did indeed have for a time a certain limited market in photography, but its poisonous properties and its relatively high price made it give place to hyposulphite of sodium. From that time it was a laboratory and pharmaceutical rather than an industrial product. But as a result of the remarkable researches of MacArthur and Forest, some fifteen years ago, in the extraction of gold by means of potassium cyanide, this salt became industrially important, giving to the whole industry of the cyanide compounds an impetus and a vitality which made it acquire rapidly its present development, which is still bound to increase.

The application of these methods brought about as an immediate consequence a considerable increase in the consumption of cyanide of potassium to such an extent that in 1898 this consumption arose to 3300 tons, and in the month of August of that year the demand was so great that the German manufactories which produce the major part of this product were unable to fill their orders punctually, notwithstanding the price had been advanced 29% to the English buyers.

In June 1899 the national bureau of foreign commerce was in possession of data from Johannesburg showing a consumption of 450,000 English pounds of cyanide per month, which amount represented a value of \$135,000, delivered.

It is quite probable that these figures would still have increased had it not been for the war in South Africa, and the consumption in that country alone would have arisen to 10,000 tons.

The result of this development is easy to foresee. The work was undertaken most zealously; the manufacturers in England and in Germany especially sought means of producing the cyanide in sufficient quantities to supply the demand, and under the most economical conditions, as shall be seen when the study of the various methods is taken up. An active struggle was established among the manufacturers of cyanide, the result of which has been infinite progress in this industry. Even at the present time numerous researches are being undertaken along these lines, and it is to be hoped that these efforts will not be fruitless, but rather a process will be found which will permit the production of potassium cyanide under conditions remunerative both to the producer and consumer. The industry of the cyanide compounds has been developed especially in Germany and in England; France has remained somewhat behind in this line. Several manufacturers produce some cyanide, to be sure, but they do not find such an outlet for it as they should have, because of the great competition in the market which the English and the Germans are making, and because of the cheaper price at which they sell their product.

This condition of affairs attracted the attention of the Minister of Commerce and Manufactures, and in a letter of Dec. 6, 1897, addressed to the President of the Council Chamber of Chemical Products, he called to the attention of the manufactur-

ers the important markets reserved for this branch of chemical industry.

The letter, as well as the discussion which it provoked at the meeting of the Council Chamber of Chemical Products on the 8th of December following, are here reproduced:

PARIS, December 6, 1897.

MR. PRESIDENT:—

The export house Orosdi Back, whose headquarters are in Paris, cité d'Hauteville, No. 9, recently called my attention to the interest which the manufacture of potassium cyanide would offer to French industry.

The use of this product in treating the wastes of gold-mines has given such results that all the mines are gradually making installations for putting this method into practice.

The present sales of potassium cyanide in the Transvaal and the whole of South Africa already exceeds 3000–4000 tons per annum, and it is expected within two or three years, when the cyanide process shall have become general, that the demand for this product will exceed 10,000 tons in the Rand district alone. If to this amount be added the quantity consumed by all the gold-mines in all parts of the world, it is seen that a considerable field is open for the sale of this product, the sale of which at present is monopolized by England and Germany.

According to Orosdi Back, the cyanide of potassium employed should be 98%, of a pale-yellow color. It is shipped in wooden boxes lined with zinc, holding 100 kg. The price varies from 190 to 230–240 francs per 100 kg. It seemed to me that the above data would be of interest to your association, and I have the honor of communicating them to you, giving you the care of making them known to the manufacturers who might be willing to use them.

Yours, etc.,

*Minister of Commerce, Industry, Post, and Telegraph.*

For the Minister, by authority.

*Director of Commerce,*

CHANDÈZE.

Council Chamber of Chemical Products, sitting of Dec. 8, 1897.

MR. PRESIDENT:—

Before receiving this letter the Minister had already interviewed me on this question, and I explained to him that the French manufacture of potassium cyanide is only enough for our needs, i.e., about 30,000 kg. per year; that this amount is produced by a single firm, other manufacturers who produced it formerly having abandoned it because of the unremunerative price obtained for it.

The price of potassium cyanide has, in fact, suffered a considerable reduction in the last few years. At present it is worth 3 francs per kg. in France, and 2.25 francs in England and Germany.

The consumption of this product is very great in the Transvaal, but the figures 3000-4000 tons, given by the firm Orosdi Back, seem somewhat exaggerated. From data which I have received, the sales in the Transvaal would amount to 100 tons per month, and only 1 ton in Madagascar; but the consumption of this colony is destined to increase.

The company in France which manufactures potassium cyanide tried to compete with foreign firms doing business in the Transvaal, but abandoned the attempt because it was estimated that the sale price of 2.25 francs per kilogram (about 22.5 cents per lb.) did not leave a sufficient profit.

MR. GASTON POULENC:—The English have found, and are now exploiting, processes for the manufacture of potassium cyanide without the use of ferrocyanide. That is a very great advantage when the net cost is considered. And this superiority will last until our manufacturers or our chemists have analogous methods.

MR. PRESIDENT:—It seems to me, finally, that the communication just presented by our fellow member fully confirms the data which I gave to the Minister, and the inability of the French industry to compete successfully at the present time.

It is to be hoped that in the near future the discoveries of our chemists will make it possible for us to regain this industry. The effort of the inventors is in this direction, and in the last dozen years, both in France and abroad, a great number of patents for the production of this substance have been taken out.

Having made these general observations, let us now examine the state of this industry in the different countries where cyanide is produced.

The following table shows the production of the different countries in 1899, according to L. Guillet:

Country.	Potassium Ferrocyanide.	Potassium Ferrycyanide.	Potassium Cyanide.
	tons.	tons.	tons.
Germany, Austria. ....	4,000	—	1,500
England. ....	3,000	—	2,000
France. ....	1,500	11	250
United States. ....	1,500	—	1,500
Belgium, Holland. ....	500	—	—
Total. ....	10,500	11	5,250

France therefore produces  $\frac{1}{21}$  of the total production of cyanides and  $\frac{1}{7}$  of the ferrocyanides, while Germany and England produce more than  $\frac{1}{2}$  of the total of these two products.

The consumption is found divided among the different countries. Ferrocyanide of potassium which is produced in France is to

a great extent exported to Germany and England, where it is transformed into the cyanide. Germany herself exports a great quantity to the United States, where for economic reasons it is transformed into the cyanide of potassium; the remainder is used at the manufactory for the various needs of the industry. The cyanide is exported to gold-mines, notably to the Transvaal, where its consumption increases daily. Thus in 1897 the consumption in the Transvaal was 1710 tons; in 1898 it had increased to 2230 tons; in 1899 to 2400 tons. The other gold districts consume but little because the beds are still worked by the old method and quite often they are not in the hands of companies or manufacturers, the gold being bought from individual workers.

However that may be, the cyanide method is gradually increasing. Several installations in the United States, in California and Alaska, have been noted, and one can foresee that gradually the total consumption will be considerably increased.

The following table gives the names of the principal firms of France and other countries which manufacture or sell cyanide compounds:



LIST OF WORKS PRODUCING CYANIDE COMPOUNDS.  
FRANCE.

Name of Firm.	Place.	Kind of Products Manufactured.
Camille Armand.....	St.-Ouen-l'Aumône (S.-et-O.)	Ferrocyanides (from purifying materials)
Dubois.....	Marseille. Works at Montolivet and Cap Janet, near Marseille	Ferrocyanides, Cyanides, Sulphocyanides
Deise.....	Paris	Sulphocyanides
Granjon.....	Marseille	of ammonium and copper
Société Nantaise de Produits chimiques.....	La Morinière, near Nantes	Ferrocyanides, Sulphocyanides
West.....	La Trinité-de-Reville (Eure)	Ferrocyanides, Cyanides
Henzel et Dubosc.....	Rouen	Copper sulphocyanide
Société Anonyme des Produits chimiques et Engrais de Birambits.....	Bègles, near Bordeaux	Ferrocyanides, Sulphocyanides
Société Générale des Cyanures.....	La Neuville, near Nancy	Cyanides
Administration des Mines de Bouxwiller.....	Genevilliers (Seine)	Ferrocyanides, Ferricyanides, Cyanides
Manufacture des Produits chimiques pour les Arts et l'Industrie. M. Tétart.....	Lyon	Ferrocyanides
Gillet.....		

GERMANY.

Name of Firm.	Place.	Kind of Products Manufactured.
Administration des Mines de Bouxwiller.....	Bouxwiller (Upper Alsace)	Prussiates, Prussian blue
Balzer & Co.....	Grunau	Potassium cyanide, Yellow prussiate
Chemische Fabrik in Billwärd.....	Hamburg	Cyanides (750 tons per annum)
J. Hauf.....	Feuerbach (Württemberg)	Sulphocyanides
Geb. Heyl & Co.....	Charlottenburg	Steel and Prussian blue
Stassfurter Chemische Fabrik vorm Vorster und Grimeberg.....	Stassfurt	Cyanides, Prussiates, Cyanate of K
Aktien Gesellschaft für Chemische Industrie.....	Schalke (Westphalia)	Prussiates
Beringer.....	Charlottenburg	
Kunheim & Co.....	Wiederschönneweide	Prussiates, Blues, Sulphocyanides of Ba, K, NH <sub>3</sub> , Al

LIST OF WORKS PRODUCING CYANIDE COMPOUNDS—Continued.  
GERMANY—Continued.

Name of Firm.	Place.	Kind of Products Manufactured.
L. Marquart.	Beuel on the Rhine	Cyanide of K, Prussiates, Sulphocyanates, Nitroprussiates
Fritz Schulz jun.	Leipzig	Prussian blue
Verkaufsyndikat der Kaliwerke Stassfurt.	Stassfurt	Cyanides, Cyanates, Prussiates, Sulphocyanides
Vossen & Co.	Neuss on the Rhine	Ferrocyanides
Zimmermann.	Weseling, near Cologne	" , Ferricyanides
Silesia Verein Chemischer Fabriken Cyanid Co.	Stoa and Marianhütte, near Sarau (Silesia)	" "
Cyanid Company.	Hamburg	" , Cyanide of K
Chemische Fabrik Pfersée Augsburg.	Pfersée, near Augsburg	" , Sulphocyanides, Cyanide of K, Sulphocyanates
Schachnow und Wolff.	Stassfurt	" , Cyanates of K, Cyanide of K
Deutsche Gold u. Silber Scheide Anstalt.	Frankfort-on-the-Main	" , Yellow prussiates
Brescius.	Rödelheim, near Frankfort	" , Sulphocyanides
Chemische Fabrik Taucha.	Taucha, near Leipsic	Cyanides of K, Sulphocyanides
E. von Haen.	List, near Hanover	Cyanides, Cyanate of K, Prussiates, Sulphocyanides
Königswärter u. Ebell.	Linden, near Hanover	Cyanides
Knoll & Co. Chemische Fabrik.	Ludwigshafen	" , Sulphocyanides
Langbein & Co.	Leipsic	" "
A. Falmer.	Freiburg	" "
Rickmann u. Rupp.	Kalk, near Cologne	" "
Schering.	Berlin	" , Ferrocyanides
Chemische Fabrik Ammonia.	Hildesheim	Prussic acid, Sulphocyanides
Luttkie u. Arndt.	Hamburg	" , Nitroprussiates
Merck.	Darmstadt	" "
J. Perl & Co.	Berlin	" "
J. Riedel.	"	" , Prussiates, Sulphocyanides
Schuchardt.	Goerlitz	Prussiates
Ludwig Pastor.	Frankfort	

LIST OF WORKS PRODUCING CYANIDE COMPOUNDS—Continued.  
GERMANY—Continued.

Name of Firm.	Place.	Kind of Products Manufactured.
Aktien Gesellsch. der chem. Producten Fabrik, Pommernsdorf.	Stettin	Yellow prussiate
Chem. Fab. Edenkoben.	Edenkoben	"
Babatz u. Wehrlen.	Rheingoenheim	"
Chem. Fab. Moenasia.	Seligerstadt	"
" " Pestchow, Davidsohn.	Dantzig	"
" " bei Karlsruhe.	Ruppritt (Bade)	"
" Prod. Fab. Altdamm.	Altdamm, near Stettin	"
S. Culp.	Barmen	"
Carl Dicke & Co.	"	"
Fab. Chem. Prod., Carl Schwede.	Frankfort	"
M. Goldschmidt.	Koepernick	"
Hemelings Chem. Ind. (Behrem).	Hemelings	"
August Klein.	Hillnhütten	"
Renan, Kessel & Co.	Cologne	"
F. A. Sapp.	Hillnhütten	"
Wesenfeld Dicke & Co.	Barmen	"
J. Bidtel.	Cologne	"
Petschow.	"	Sulphocyanide

ENGLAND.		
Name of Firm.	Place.	Kind of Products Manufactured.
British Cyanides Company.	London	Cyanides and Ferrocyanides
Cruickshank.	Birmingham	"
Dolbe & Son.	Sheffield	"
Foster & Son.	Leeds	"
Harris & Co. Limited.	Birmingham	"
Hopkins & Williams.	London	"
Johnson & Sons.	"	"

LIST OF WORKS PRODUCING CYANIDE COMPOUNDS—Continued.  
ENGLAND—Continued.

Name of Firm.	Place.	Kind of Products Manufactured.
Johnson Matthey & Co., Limited.	London	Cyanides and Ferrocyanides
Jones.	"	"
Rugby.	Walsall	"
T. Savage.	Birmingham	"
W. Savage.	"	"
Sheffield Chemical Company.	Sheffield	"
The Standard Cyanides Manufacturing Company, L't'd	London	"
Wilkinson & Son.	Sheffield	"
Palfair.	Clyde Bank	"
London Gas Company, Beckton & Co.	London	Sulphocyanides
Hurllett.	Glasgow	Prussiates
The United Alkali Company.	Liverpool	"
Cassel Gold Extracting Company.	Glasgow	Cyanides
May and Baker.	London	"
Scottish Cyanides Company.	Leven	"

## UNITED STATES.

Name of Firm.	Place.	Kind of Products Manufactured.
The Rossler, Haslachner Co.	New York	Cyanides
American Cyanides Manufacturing Company.	Trenton	"
Philadelphia Ammonia Company.	Philadelphia	"
Baltimore Chrome Works.	Baltimore	"
Bower & Son.	Philadelphi	"
Carthuff.	Newark	"
Tikenbrach Chemical Company.	Hoboken	"
Krems & Co.	Chicago	"
Newark Chemical Company.	Newark	"
V. H. Davis Chemical Works.	New Bedford	" and Prussiates

## LIST OF WORKS PRODUCING CYANIDE COMPOUNDS—Continued.

## BELGIUM.

Name of Firm.	Place.	Kind of Products Manufactured.
C <sup>e</sup> Belge des Produits Chimiques "La Senne" . . . . .	Brussels	
A. Dupont & Co. . . . .	Haaren-lez-Brussels	
Ch. Lemm. . . . .	Antwerp	
De Poorter (Lemaire & Co.) . . . . .	Gand and Læcken	
Produits Chimiques spéciaux. . . . .	Antwerp	

## AUSTRIA-HUNGARY.

Name of Firm.	Place.	Kind of Products Manufactured.
Hochstetter & Schickardt. . . . .	Brunn	Prussiates
Rötlingshöfer. . . . .	Brosdow, near Cerkowitz	"
Engel und Becker. . . . .	Prague	Sulphocyanides

## HOLLAND.

Name of Firm.	Place.	Kind of Products Manufactured.
Van der Elst & Matthies. . . . .	Amsterdam	Sulphocyanides
Van Veen & Co. . . . .	Bussum	Prussiates
Société anonyme des Produits chimiques. . . . .	Buremonde	"

## RUSSIA.

Name of Firm.	Place.	Kind of Products Manufactured.
Agthe Frey & Co. . . . .	Riga	Prussiates
Prokunin & Petrowsky. . . . .	Sosnoska	"

Although it is extremely difficult to obtain data from the manufacturers concerning the production and consumption, the net cost, etc., we have, nevertheless, been able to procure a certain number of documents bearing on these questions. The following tables give a sufficiently correct idea of the condition of the cyanide industries, and show well the development of this branch of chemical industry during the past few years.

**FRENCH IMPORTATIONS OF POTASSIUM FERROCYANIDE IN KILOGRAMS.**

Year.	Exporting Country.				Total.	Value.
	England.	Germany.	Belgium.	Other Countries.		
1887.....	168,669	—	168	79,512	248,349	347,689
1888.....	186,404	—	—	77,784	264,288	343,574
1889.....	150,028	—	65	66,660	216,753	303,454
1890.....	48,086	—	65,317	38,777	152,180	243,488
1891.....	100,932	—	28,310	15,725	144,967	260,941
1892.....	69,354	—	52,185	20,018	141,557	254,803
1893.....	50,771	—	62,761	19,529	133,061	239,510
1894.....	40,079	—	42,798	31,173	114,050	216,695
1895.....	78,547	—	23,079	20,956	122,582	232,906
1896.....	48,501	—	49,768	4,482	142,751	228,402
1897.....	29,178	11,454	54,736	1,216	96,584	125,559
1898.....	37,266	9,153	18,457	84	64,960	87,696
1899.....	—	15,754	40,243	50	56,047	86,873
1900.....	1,654	12,789	41,700	—	56,143	92,636
1901 (10 months).	—	—	—	—	113,700	149,000

**AMOUNTS CONSUMED IN EACH OF THESE EXPORTING COUNTRIES.**

Year.	England.	Germany.	Belgium.	Other Countries.	Total.	Value.
1887.....	89,398	—	141	62,220	151,759	—
1888.....	104,354	—	52	76,699	181,105	—
1889.....	84,458	—	65	62,701	147,224	—
1890.....	48,086	—	40	11,477	81,822	—
1891.....	69,354	—	353	14,212	73,492	—
1892.....	50,771	—	379	16,489	83,919	—
1893.....	40,079	—	9,887	782	67,639	—
1894.....	77,447	—	27	15,705	50,478	—
1895.....	48,501	—	6,441	32,883	92,879	—
1896.....	—	—	—	—	87,825	—
1897.....	28,939	8,460	29	336	33,764	49,093
1898.....	—	—	—	—	15,363	20,470
1899.....	—	—	—	—	12,022	18,634
1900.....	—	—	—	—	13,272	21,899
1901 (10 months).	—	—	—	—	90,200	149,000

# 80 THE PRESENT CONDITION OF THE CYANIDE INDUSTRY.

## FRENCH EXPORT OF POTASSIUM FERROCYANIDE IN KILOGRAMS FROM 1897-1900.

Country.	1897	1898	1899	1900
England.....	45,339	115,531	87,470	71,444
Germany.....	41,878	59,236	171,139	451,934
Belgium.....	41,879	—	49,017	47,272
Switzerland.....	—	22,293	—	29,229
Italy.....	—	—	—	17,185
Other countries.....	25,136	27,933	55,580	26,168
Colonies and Protectorates	5,481 of which 2,189 for Algeria.	21,761 of which 20,000 for Reunion.	3,673	3,415
United States.....	147,658	265,796	55,917	—
Spain.....	—	—	40,328	—
Total.....	307,371	512,550	463,124	645,697
Value in francs.....	403,557	697,996	717,842	1,065,400

## TOTAL FRENCH AND FOREIGN EXPORTATION OF POTASSIUM FERROCYANIDE, 1887-1896.

	1887	1888	1889	1890	1891
Amount in kilograms..	122,048	90,426	85,594	127,384	188,628
Value in francs.....	177,083	118,789	122,898	215,397	363,044

	1892	1893	1894	1895	1896
Amount in kilograms..	120,696	184,231	198,769	107,974	139,735
Value in francs.....	230,074	361,350	406,797	216,986	232,014

## FRENCH AND NATIONALIZED EXPORTATION OF POTASSIUM FERROCYANIDE, 1887-1896.

	1887	1888	1889	1890	1891
Amount in kilograms..	24,867	6,175	15,334	57,912	117,571
Value in francs.....	41,030	9,263	24,534	104,242	235,142

	1892	1893	1894	1895	1896
Amount in kilograms..	64,092	118,938	145,682	78,907	84,383
Value in francs.....	128,184	243,823	305,932	161,759	143,451

## PART THREE.

### METHODS OF MANUFACTURING CYANIDE COMPOUNDS.

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#### GENERAL CONSIDERATIONS.

BEFORE taking up the discussion of the numerous methods for the manufacture of the cyanide compounds, it seems necessary to glance for a moment at the evolution accomplished by these methods, a very interesting evolution, since it has transformed an industry which was at first entirely subjected to the crudest empiricism to an industry based on purely scientific data.

The industry of the cyanogen compounds, like that of the greater part of the chemical industries, had its origin in alchemy. It originated in 1704, from the discovery of Prussian blue. This discovery, which was purely accidental, is due to the Berlin dyer Diesbach, who obtained this compound by the action of alum and sulphate of iron on the potash residues which the then celebrated alchemist Dippel had used in the rectification of an animal oil extracted from the volatile substances of blood.

From this discovery, Dippel concluded that Prussian blue was formed by the action of iron on potassa which had been brought in contact with organic animal substances at a certain temperature.

The discovery of Diesbach immediately became of industrial importance, and Prussian blue was prepared by calcining dried beef's blood, and later meat or horns with potassium carbonate.

The product of this treatment was extracted with water, and the solution thus obtained, called *blood-lye*, was treated with alum and sulphate of iron, giving Prussian blue. This was for a long



time the only body known and prepared, and this without knowing exactly what was its composition and its mode of formation.

In 1752 Macquer, then Bergmann and Sage, showed that from Prussian blue a definite and crystallizable salt could be extracted, the nature of which they could not determine.

That Prussian blue and the salt obtained from blood-lye were compounds of cyanogen was first definitely proven in 1823 by Gay-Lussac.

Although this was an important discovery, yet the methods of producing these compounds were not at all changed, and for a long time the only method employed, notwithstanding its imperfections, was that of igniting nitrogenous organic substances in the presence of alkaline carbonates. That method sufficed, moreover, to supply the limited demand.

But, beginning with 1837, a most interesting and important series of discoveries and researches in the history of the cyanide industry attracted the attention of investigators and manufacturers, and fixed in a clearer manner the ideas which were being formed concerning the formation of these bodies. The successive discoveries of Clark and of Redenbacher, describing the formation of efflorescences of potassium cyanide in blast-furnaces, together with the works of Lewis Thompson, Desfosses, Fownier, and Young, who obtained this same compound by the action, at red heat, of a current of air upon a mixture of potassium carbonate and charcoal, gave birth to the first principles of a theory which at first was disputed, but soon after acknowledged to be the true one.

In fact, several years later, Bunsen, then Playfair, and later Riecken, in their investigations established clearly the rôle which atmospheric nitrogen plays in the formation of cyanide compounds.

It is easy to understand how this discovery attracted the attention of the manufacturers when the importance and the economic aspects of the question are considered. From that time on they exerted themselves in applying in a practical way the results obtained by investigators, and numbers of patents followed each other, all tending to do away with the use of nitrogenous organic matter (which is rather costly and imperfect) and approaching as much as possible to the synthetic production, which is simpler and more economical.

At the present time the tendency is still in the same direction, and one must not despair of seeing, in the very near future, the success of this important problem of the fixation of atmospheric nitrogen in the production of cyanide compounds on an industrial scale.

The first efforts in this direction were unfortunately fruitless and therefore short lived. They were all inspired with the same idea: the passing of nitrogen over a suitably heated mixture of charcoal and an alkaline carbonate or an alkali. Such are the methods of Bunsen, Ertel, Armengaud, Possoz, and Boissière, Lambilly.

The next step was the replacing of the carbonates of the alkalis by the alkali metal itself (Castner, MacDonald, Mackey, Hornig, Schneider).

Other inventors made use of ammonia instead of nitrogen. Quite recently, in Germany, processes have been patented along this line, and, as will be seen later, the results are thought to be satisfactory.

Indirect means were also tried, such as those suggested by Gelis, and taken up by Tcherniac and Gunzberg, which consisted in producing ammonium sulphocyanide, and this was converted into potassium cyanide.

In the mean time the discovery of cyanide compounds in the purifying masses from the manufacture of illuminating-gas, and in sugar-beet molasses and vinasses, added a new and lively interest to this industry.

One must also mention the use of metallic carbides recently praised as a means of fixing atmospheric nitrogen for the production of cyanides, a tentative method which seems to have given some results.

That the question is complex may easily be seen from these general remarks. It has not yet been definitely solved, nor has the ideal process been found. Nevertheless certain modes of manufacture have already furnished appreciable results, and show a real progress. All these will be reviewed in this portion of this work.

The order in which this interesting study will be taken up follows quite naturally from the preceding remarks and will be as follows:

#### Chapter VI. Manufacture of Cyanides.

- (1) Non-synthetic processes: (a) production by means of ferrocyanides; (b) production by means of sulphocyanides.

- (2) Synthetic processes: (a) the use of atmospheric nitrogen;  
(b) the use of ammoniacal nitrogen.

## Chapter VII. Manufacture of Ferrocyanides.

- (1) Old processes.
- (2) Extraction of gas residues: (a) direct extraction of the gas; (b) extraction of ammoniacal liquors; (c) extraction of the spent oxides from illuminating-gas.

## Chapter VIII. Manufacture of Ferricyanides.

## Chapter IX. Manufacture of Sulphocyanides.

**Chapter X. Manufacture of various other cyanide compounds:  
nitroprussiates, Prussian blue, Turnbull blue, etc.**

## CHAPTER VI.

### MANUFACTURE OF CYANIDES.

#### I. NON-SYNTHETIC PROCESSES.

##### A. EXTRACTION OF CYANIDES FROM FERROCYANIDES.

**Old Process.**—The oldest method of obtaining potassium cyanide, a method which is scarcely ever used except in the manufacture of the absolutely pure salt, is that of Robiquet, modified by Geiger. It consists in igniting the dried yellow prussiate or ferrocyanide of potassium.

Under the influence of heat the ferrocyanide of potassium is decomposed according to the reaction



It is absolutely essential that the ferrocyanide of potassium used for this purpose should be (1) perfectly free of sulphate of potassium, which in the above reaction would become transformed into the sulphide, which would give a yellow color to the cyanide; (2) perfectly free from its water of crystallization, which would tend to retard the reaction.

The method of preparation is as follows: Yellow prussiate is first carefully dried at about 100° C. upon plates of sheet iron or in cast-iron pans; thus the dried product is transferred to forged-iron crucibles capable of holding about 80 liters and covered with an iron lid. These crucibles are then placed in batteries of five or six in furnaces.

Into each one are placed 80 kilograms of ferrocyanide and the whole gradually heated. Just as soon as the product is fused, the temperature is gradually raised to a dull red; the whole is stirred

from time to time with a long-handled iron dipper. The operation lasts about seven or eight hours, and is ended when a sample taken out and cooled has a white, dull, porcelain-like appearance.

Care must be taken that the temperature does not go beyond dull redness, otherwise the cyanide formed would itself be decomposed into potassium carbide and nitrogen.



When the operation has been carefully carried out, the result is a mixture of carbide of iron and cyanide of potassium, the former adhering to the sides of the crucible, the latter in the midst of the mass.

In order to obtain the cyanide from the mixture recourse may be had to decantation followed by filtration or to lixiviation.

In the first case the fused product is decanted upon cast-iron filters (*A*) (Fig. 1), the bottom of which is a grate which is covered to about  $\frac{1}{3}$  of the height of the filter with iron turnings. This filter is kept at dull redness during the time of the operation. The cyanide is drawn from the crucibles by means of iron dippers and poured upon the filter. The first portions of the filtrate are often contaminated with carbide of iron; they are therefore fused anew in the crucibles and there refiltered.

The filtrate is collected in polished and perfectly clean iron pans (*C*), which are set in a trough (*D*) filled with cold water.

Too long contact of the potassium cyanide with the iron carbide formed must be avoided, for experience has shown that the ferrocyanide was inclined to become once more formed by an inverse reaction.

If recourse is had to lixiviation, the product of ignition is taken up either with water or with alcohol.

The extraction with water is a cheaper but a more delicate operation. Much care must be taken and the work carried on rapidly, because water always decomposes the potassium cyanide, forming ferrocyanide.

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\* It may be remarked that it is precisely this decomposition of potassium cyanide at a high temperature which renders it impossible to obtain the cyanide by means of the electric furnace, as was attempted by Moissan.

Although the use of alcohol is quite costly, it is preferable. The extraction is carried on in the warmth; it is quite slow because of the little solubility of potassium cyanide in alcohol.

In each of the above cases, the lixiviation is followed by evaporation and a rapid drying of the cyanide. In the case of alcohol this solvent may be recovered and so be used over and over.

As may be seen this process is rather defective. During the process notable quantities of cyanogen in the form of iron carbide and nitrogen are lost, and in fact only about  $\frac{2}{3}$  of the cyanogen used is recovered; 10 parts of ferrocyanide give only 7 parts of

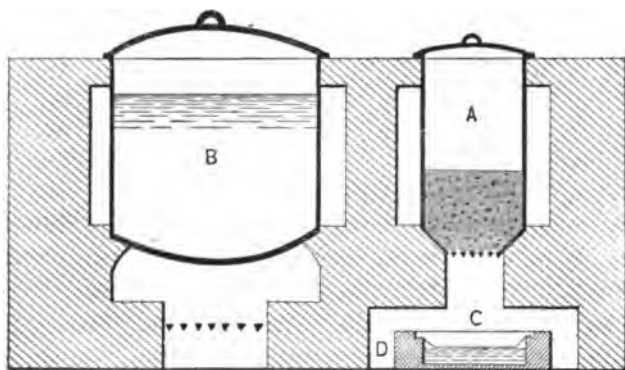


FIG. 1.—Cyanide-filter.

cyanide, i.e. 45 kg. of absolutely pure cyanide for 100 kg. ferrocyanide used.

**Liebig's Process.**—With a view of remedying this objection, Clemm Rodgers and later Liebig proposed igniting dry ferrocyanide in the presence of dry potassium carbonate. This process is still sometimes used. Clemm advised the use of a mixture of 8 parts ferrocyanide and 3 parts potassium carbonate. The reaction is as follows:

(1)  $\text{Fe}(\text{CN})_6\text{K}_4 + \text{CO}_3\text{K}_2 = 6\text{CNK} + \text{FeO} + \text{CO}_2$ , but under the influence of the iron oxide formed a small quantity of cyanide is transformed into cyanate, so that the reaction is in reality as follows:

(2)  $\text{Fe}(\text{CN})_6\text{K}_4 + \text{CO}_3\text{K}_2 = 5\text{CNK} + \text{CNOK} + \text{Fe} + \text{CO}_2$ , or, better still, a combination of equations (1) and (2).



The product is treated with water whereby a solution is obtained consisting of cyanide and an excess of potassium carbonate.

In order to separate these bodies, alcohol or acetone is added which precipitates the insoluble cyanide.

The residue, consisting of iron oxide, potassium carbonate, iron, small quantities of undecomposed ferrocyanide and unprecipitated cyanide, is powdered and allowed to stand in air. Under these conditions insoluble iron peroxide is formed. The product is once more extracted, the solutions evaporated, and the residue ignited. In this way a certain part of the potassium carbonate may be recovered which may be used over again. Ten parts of ferrocyanide give 8.8 parts cyanide and 2.2 parts of cyanate.

**Wagner's Process.**—In order to avoid the formation of cyanate at the expense of cyanide, Wagner proposed igniting the mixture of ferrocyanide and alkali carbonate with a small quantity of finely pulverized wood charcoal the use of which is to reduce any cyanate formed. The following are the amounts proposed by Wagner:

Ferrocyanide of potassium.....	8	parts.
Carbonate of soda.....	2	"
Powdered wood charcoal.....	0.2	part.

The reaction is



Another advantage of this method would be the separation of iron, which would be easier. The mixture thus obtained is formed by 4 mol. of potassium cyanide and 2 mol. sodium cyanide. Later will be discussed the advantage which this mixture, which is richer in cyanogen, has over potassium cyanide alone.

**Chaster's Process.**—This is only a modification of Wagner's process, and consists in adding to the mixture of ferrocyanide carbonate and charcoal a certain amount of tar, pitch, or bitumen. The yield is thus somewhat greater, the reaction being carried on in the reducing atmosphere produced by the hydrocarbons added.

The following are the proportions proposed by Chaster:

Anhydrous ferrocyanide.....	65-75	parts.
Carbonate.....	20	"
Wood charcoal.....	5	"

The ferrocyanide and carbonate are ground together and during the grinding 5% dried wood charcoal is added, together with a quantity of tar, pitch, bitumen, or asphaltum or any other analogous substance sufficient to give the whole mass the consistency of a paste or of mortar. In case the mass may not be plastic enough a small quantity of benzine or petroleum is added.

This mass is compressed into the form of briquettes, which are ignited in a furnace with a reducing flame.

Notwithstanding these modifications, processes which are based on the decomposition of ferrocyanide under the influence of heat are not profitable. They are rather costly; the losses in nitrogen, in alkali, and even in cyanide by volatilization are sometimes considerable.

Their industrial use has always been most limited. In trying to perfect these processes, many very ingenious modifications have been devised which have, it seems, given good results, and the industrial use of which has, latterly, been quite extensive.

**The Process of Rossler and Hasslacher** (of New York).—The type of these new modifications is that of the house of Rossler und Hasslacher of New York, belonging to the Deutsch Gold und Silber Scheide Anstalt. This process, which was proposed by Erlenmeyer, is based upon the action of metallic sodium on potassium cyanide, according to the reaction



The product is then treated with water and the solution evaporated.

The product thus obtained, which is sold as potassium cyanide 98–100%, is in fact but a mixture of 4 mol. of potassium cyanide with 2 mol. sodium cyanide, a product identical with that produced by Wagner's process. If the whole be assumed as potassium cyanide, it is seen that it contains 98% of the cyanogen used. Moreover, this mixture has the advantage of being richer in cyanogen than is the potassium cyanide, because the atomic weight of sodium is less than that of potassium. Thus 109 grams of this mixture corresponds to 106 grams of potassium cyanide.

Besides having the advantage of avoiding loss of cyanogen, this method permits the use of metallic sodium, a metal which, since



Deville's process for the manufacture of aluminium was abandoned, found but little use in the arts.

At present, sodium is produced on a large scale by electrochemical industries; it is therefore of interest to call attention to this method of application. This process is, moreover, in considerable use in England, Germany, and even in France.

**Wichmann and Vautin's Process.**—Because sodium was still rather expensive, attempts were made to replace it with alloys of alkali metals with lead. These alloys are at the present time obtained much cheaper than the alkali metals, by subjecting fused alkali chloride to electrolysis in a bath of melted lead, which acts as a cathode.

In order to obtain potassium cyanide, a mixture of potassium ferrocyanide with a lead-potassium alloy is used. If the sodium cyanide be desired, sodium ferrocyanide and a lead-sodium alloy are taken.

As in the Rossler and Hasslacher process, a double cyanide of sodium and potassium may be prepared, by causing an alloy of lead sodium to act upon potassium ferrocyanide, or a lead-potassium alloy to act upon sodium ferrocyanide.

The dehydrated ferrocyanide is first pulverized and then mixed with the powdered alkaline alloy. The grinding of these alloys is easy enough, because they are generally brittle. Ordinarily the grinding is done in the presence of a small quantity of mineral oil, the use of which prevents oxidation.

The mixture is fused in furnaces at as low a red heat as possible. This fusion should, of course, be done out of contact with air. When the reaction is finished, there remains a fused mass consisting of cyanide as well as iron and spongy lead.

These two foreign substances are separated from the cyanide by decantation or by filtration. The mass may likewise be treated with water, and after filtration the solution of cyanide may be evaporated. The lead and the iron may also be separated. In order to do this, the mixture is melted on an inclined plane, when the lead, which is more fusible, runs off first, leaving the iron behind, or else the mixture is finely divided and stirred in a bath of melted lead, which retains the lead which was mixed with the iron, thus permitting the iron to be collected. This iron may then serve in the prepa-

ration of ferrocyanides. The lead is itself used anew in the preparation of the alkaline alloy.

The proportion of ferrocyanide to alloy to be used depends on the quantity of alkali metal which the alloy contains. The authors claim that, in practice, an alloy containing 10% of alkali metal is the best adapted. It is, however, always better to use a somewhat larger quantity than is theoretically sufficient in the substitution of the alkali metal for the iron of the ferrocyanide. In practice, in order to prepare a double cyanide of sodium and potassium, 10 parts by weight of the dehydrated potassium ferrocyanide and 13 parts of the 10% lead-sodium alloy may be used.

A modification of this process has been proposed by Hetherington, Hurter, and Muspratt (English patent March 20, 1894, March 1895); it consists in melting the alkaline alloy under a certain thickness of cyanide obtained in a previous operation, and adding to this mixture, in small portions, the dried ferrocyanide. These inventors recommend using an alloy with 13% sodium. When the reaction is complete the final product is found in three separate layers—melted lead, reduced iron, and alkalicyanide, which are easy of separation. The lead-sodium alloy may be replaced by the lead-potassium alloy, but the former is preferable.

Does the use of alkaline alloys possess, as stated by the inventors of various patents on this subject, a distinct advantage over the use of alkali metals alone? This question is not so easily answered. It cannot be denied, in view of the ease with which the alloys are obtained, that the potassium-lead alloys, and more especially the sodium-lead alloys, are much cheaper, all things being equal otherwise, than the same alkali metals themselves. From this point of view the processes of Vautin and Hetherington would possess advantages. But, on the other hand, one has a right to ask, What is the rôle played by the lead in these reactions? It is known that lead has but a slight affinity for the cyanides, and that is the reason why lead cyanide has never been prepared.

The use of alkali cyanides has even been praised as a means of reducing lead carbonate to the metallic state. It becomes evident, therefore, that in the action of lead-sodium alloy on alkali ferrocyanide, sodium alone enters into the reaction.

Since the content of the alkali metal in the alloys is generally

about 13%, in order to produce the same result as 100 parts of sodium one must use 770 parts of the lead-sodium alloy. Therefore the net cost of lead-sodium alloys containing 13% sodium should be 7.7 times less than that of metallic sodium, in order that such processes as those of Vautin and of Hetherington, etc., may possess pecuniary advantages over those processes represented by Rossler-Hasslacher, etc. The cost of the alloy must, indeed, be even cheaper, because in the first processes one must also reckon the expenses due to the separation of the iron and the lead in order to recover the latter. Now then, according to data on this subject, the price of lead-sodium alloys containing 12-15% sodium is not so low, in fact it is only one fifth of the price of metallic sodium, the price of sodium taken into account being that made especially to manufacturers of cyanides.

It would seem, moreover, that the advantage in using alkali alloys is rather in the case of working and manipulating the products. In this case, one must assume that the lead is either a reducing agent preventing the formation of cyanates, or simply a diluting agent (when it is considered that it forms 87% of the alloy) whose rôle would be to prevent the sodium from floating on top of the mass of melted ferrocyanide and thus not enter the reaction.

In these two cases the advantage offered by the alkali alloys would be especially valuable from the point of view of the yield in cyanide.

**Dalinot's Process.**—This also depends on the action of an alkali metal on ferrocyanide, but in this case the metal is no longer used in the free state; it is produced in the nascent state during the reaction.

In a suitable vessel, and at the required temperature, place dried ferrocyanide mixed with sodium hydroxide or with potassium hydroxide in as dry a state as possible. To this mixture add finely pulverized calcium carbide. The ingredients should be added in atomic proportions.

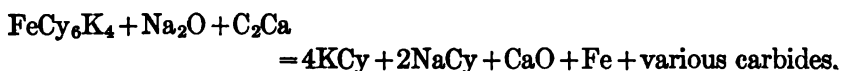
As is well known, calcium carbide possesses remarkable reducing properties. Under the conditions just mentioned it acts upon the only body containing oxygen, that is the alkali, and sets the metal free.

This reaction is the result of the well-known fact that sodium

unites with oxygen, producing  $\text{NaO} + 100$  calories, while calcium combines with oxygen, forming  $\text{CaO} + 135$  calories. Consequently the calcium removes the oxygen from the sodium hydroxide, leaving lime and metallic sodium.

The sodium is found in the mass in the molecular state. It comes in contact with the cyanogen which was united to the iron, and which has been set free in consequence of the ignition of the ferrocyanide.

In accordance with the law that the most stable body is the one first formed, sodium cyanide is produced, the reaction being

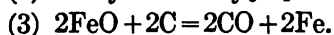
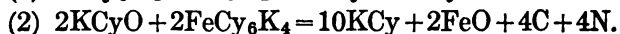
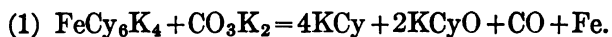


During the operation an energetic stirring of the fused mass is maintained so as to have perfect contact. When the operation is over, the fused mass is filtered through a hot filter in order to separate the residue of iron and lime.

Instead of the caustic alkalis, the alkali carbonates may likewise be used.

The calcium carbides should be quite dry. For this purpose it is ground in a grinder whose interior is perfectly sheltered from the atmosphere, and is in air-tight communication with a reservoir containing sulphuric acid. This procedure does not lack in originality, but its working does not seem to be very practical. It is quite difficult, in fact, to obtain an alkali completely free of water, whence comes a loss in cyanide compounds under the form of ammonia. On the other hand, calcium carbide of commerce is frequently impure and gives to the cyanide a more or less intense coloration, injuring the commercial value of this product.

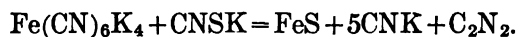
**Adler's Process.**—This process was patented in July, 1900, and is but an improvement on that of Liebig. With the object of reducing the cyanates, Adler no longer employs charcoal but alkali ferrocyanides according to the reaction:



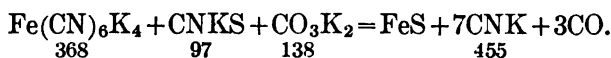
368 parts of dry ferrocyanide of potassium are fused with 138 parts of dry potassium carbonate, and toward the end of the reaction 736 parts of dry ferrocyanide are added a little at a time. An abundant froth produced by the reaction of the cyanate is at first formed.

When the mass is in a tranquil fusion, it is filtered in order to separate the cyanide formed from the impurities—iron, oxide of iron, etc.

**Etard's Process.**—This process is connected rather with the extraction of cyanides from sulphocyanides, since it consists in removing the sulphur of the sulphocyanides by means of the iron of the ferrocyanides according to the reaction



In practice the perfectly dry ferrocyanide is fused with the equally dry sulphocyanide. Sulphide of iron is formed, which is deposited during quiet fusion. The cyanide formed is decanted hot; the cyanide gas which is set free is not lost, but collected in an alkaline solution. The mass may likewise be taken up by water, methyl alcohol, or ethyl alcohol. In the first case, work is carried on as rapidly as possible out of contact with air, in order to avoid the formation anew of the ferrocyanides. In order to avoid the formation of the cyanide gases and consequently to increase the yield, carbonate of potassium may be added to the mixture of ferrocyanide and sulphocyanide. The reaction is then as follows:



In this wise, 7 molecules of cyanide of potassium are obtained instead of 5 molecules, as in the previous reaction.

**Bergmann's Process.**—This process, which is one of little practical value, and which produces only the cyanides of copper and silver, is a wet method.

It consists in heating a solution of ferrocyanide in the presence of a copper or a silver salt, in sufficient quantity to effect the total union of the cyanide of the prussiate with the copper or the silver.

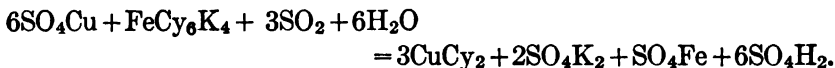
The mixture should contain a certain proportion of free acid, which, producing the decomposition of the ferrocyanide, causes the formation of prussic acid, which unites with the silver or with the copper to form cyanides of these metals.

In the case of the cyanide of silver the reaction is as follows:



422 parts by weight of crystallized ferrocyanide of potassium are dissolved in 50 times its weight of water, to which is added a 2% solution of 1020 parts of nitrate of silver. After slightly acidifying with sulphuric acid, the solution is brought to a boil until the whole of the precipitate of ferrocyanide of silver which is first formed is completely transformed into cyanide of silver by absorbing the whole of the silver remaining in excess. This cyanide is separated by decantation and washings.

In the case of the copper cyanide the reaction may be expressed thus:



In order to avoid a too excessive action of the 6 molecules of free sulphuric acid which are formed in the course of the reaction it is well to operate in very dilute solution, or to neutralize the acid as fast as it is formed by the addition of alkali. Likewise a sulphite may be used from the beginning. At first a reddish-brown precipitate of ferrocyanide of copper is formed, which under the action of heat is gradually transformed into a white, flucculent cyanide of copper.

The cyanide of copper thus obtained furnishes very interesting double cyanides when digested in the cold with an alkaline sulphide.

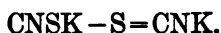
#### B. EXTRACTION OF CYANIDES FROM SULPHOCYANIDES.

Sulphocyanides have but a very limited market. They constitute, as will be seen later, one of the most important residues in the manufacture of illuminating-gas. Moreover, for a certain time, they formed the basis of several methods of cyanide manufacture,

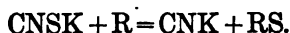
due to the remarkable works of Caro, Conroy, and of Playfair, who demonstrated that they could be a profitable source of cyanide production.

Thus, for a long time, attempts have been made to transform these salts into cyanides or into ferrocyanides, which find a more extended application. The interest taken in this subject is well shown by the numerous studies, and the various patents taken.

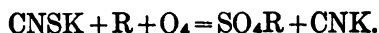
Theoretically, this conversion of sulphocyanides into cyanides appears quite simple. If the formula of sulphocyanide of potassium is taken, for example, one sees that its conversion into cyanide is made by the simple removal of the atom of sulphur which it contains:



There are two general methods which may be used in producing such a result. The first is one of reduction, in which case a sulphide is formed



The second, on the contrary, consists in removing the sulphur by oxidizing it with production of a sulphate:



## I. METHODS OF OXIDATION.

This method of treatment is the oldest, but it has never been used on an industrial scale.

The first attempt along this line was made by Hadow, who used permanganate of potash and peroxides of lead and manganese. In a method for the determination of sulphocyanides by means of permanganates, Erlenmeyer showed that in an acid solution the reaction takes place quantitatively:



This method is entirely demonstrated, but the high cost of permanganate was a serious obstacle to its industrial application. Nevertheless, this discovery of Erlenmeyer caused an awakening of

ideas. Alt showed that in the presence of barium chloride, using  $\text{HNO}_3$  as oxidizing agent, the reaction is likewise quantitative.

The ingenious attempts of Parker and of Robinson (1888-1889) must also be mentioned. The latter made use of electrolysis. He passed the electric current through a solution of sulphocyanide in sulphuric acid. Prussic acid,  $\text{CNH}$ , was formed, which was collected in an alkaline solution. The causes of failure of such processes may be easily understood. The prussic acid set free was a continual source of danger to the employes on account of its great toxicity.

**Raschen's Methods.**—The next attempt was the use of nitric acid as oxidizing agent under certain fixed conditions. Such are the processes of Raschen and Brock, worked by The United Alkali Co., Limited. To the kindness of Dr. J. Raschen, Director of The United Alkali Co., Limited, we owe a complete description of his processes, which is reproduced in full. In the first of these processes the line of procedure, as indicated in the patents taken out by Brock and Raschen (1888, 1895, 1896), is as follows: A 20-30% solution of dry sodium or calcium sulphocyanide is used. A definite quantity of hot water, or, better still, of mother-liquor from a previous operation, is placed in a hermetically closed boiler provided with a stirrer and the solution is heated to  $96^\circ$ . The stirrer is then set in motion while at the same time the solution of sulphocyanide and nitric acid are added. The addition of these two solutions must be so regulated that there is always a slight excess of the acid in the mixture. The whole of the sulphur of the sulphocyanide is oxidized into sulphuric acid, while at the same time a mixture of nitrous acid, water-vapor, nitrogen oxide, carbonic acid, and hydrocyanic acid is set free. These acids are passed through a scrubber containing water at  $80^\circ \text{C.}$ , which absorbs the nitrous acid. After having undergone this first purification and having been cooled, the gaseous mixture passes into an absorption apparatus divided into two compartments. The first contains cold water, which absorbs a great portion of the hydrocyanic acid, allowing the carbonic acid and the nitrogen oxide to pass on; the second contains milk of lime, which retains the carbonic acid and the remainder of the hydrocyanic acid, so that at the outlet of the apparatus, nitrogen oxide escapes, which, mixed with air, is recovered under the form



of nitric acid, capable of being used again in the same process. The solution of calcium cyanide in the second compartment is filtered from the precipitate of the carbonate of lime and converted into alkali cyanide by double decomposition. The solution of hydrocyanic acid in the first compartment is neutralized by means of an alkaline solution, forming an alkali cyanide. The cold water of the first compartment may equally well be replaced by an alkaline solution. It is of the utmost importance that the operation be carried on absolutely out of contact with air, otherwise the nitrogen oxide, would become oxidized with the formation of nitrogen peroxide, which latter would be absorbed by the alkaline solution, forming nitrite and nitrate, which would contaminate the cyanide and so be a serious hindrance to the fusion of this compound, the mixture of cyanide and nitrate reacting with violence.

It is likewise necessary because of the extreme toxicity of the prussic acid to work very carefully and to maintain a slight vacuum in the apparatus, so that no gas shall escape into the air if the apparatus should leak.

Raschen and Brock modified this process by using mineral oxidizing agents, such as the nitrates, chromates, peroxides of lead or of manganese in the presence of sulphuric acid. With the water is mixed the acid and the oxidizing agent and the whole brought to a boil; then is added, little by little, the sulphocyanide dissolved in water. It is necessary to use a somewhat larger quantity of oxidizing agent and acid than the theoretical amount indicated by the following reaction, using sulphocyanide of sodium as an example:



Toward the end a little more heat is applied in order to drive off completely the whole of the hydrocyanic acid. The gaseous mixture is collected and purified, as before. In the Wigg works at Runcorn, which belong to The United Alkali Co., Limited, this process slightly modified is in use at the present time on a large scale.

Raschen and Brock have, in fact, found that better yields (96%–99% of theoretical) are obtained if more dilute solutions be used (170 grams per liter), and if the solution of sulphocyanide be poured

slowly into the dilute and boiling nitric acid. At Runcorn sodium sulphocyanide is used, besides sodium nitrate and sulphuric acid, which latter act as oxidizing agent.

The apparatus used in the decomposition consist of stoneware carboys  $A_1, A_2, A_3, \dots A_n$ , placed in series, connected with each other by means of earthenware tubes starting at about mid-height of one carboy and ending in the next at the bottom. Each one of them carries, besides, an outlet tube  $B$  and a tube  $C$  for the inlet of the steam, which latter tube serves as stirrer.

First the carboys are filled with dilute sulphuric acid, then steam is let on so as to reach nearly the boiling-point. Then the solutions of sulphocyanide (170 grams per liter) and sodium nitrate are run in simultaneously. The letting in of steam and of solutions is so regulated that the temperature always remains constant, and the liquid passing from the first into the second carboy no longer contains traces of sulphocyanide, and the liquid of the last carboy is free from hydrocyanic acid. The gases which are liberated are chiefly hydrocyanic acid and nitrogen dioxide together with a little carbonic acid, nitrous acid, and considerable amounts of water-vapor. The gases pass first into the tower  $D$ , filled with quartz

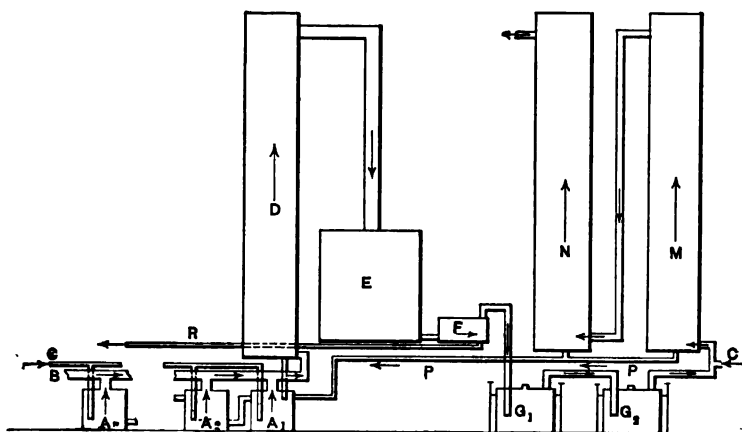


FIG. 2.—Raschen's Apparatus.

pebbles, through which they pass from bottom to top, where they meet a shower of cold water circulating in the opposite direction,

which absorbs the oxides of nitrogen, without absorbing the hydrocyanic acid, because the temperature has not been lowered. The water-vapor is condensed in an ordinary condenser *E*; it carries with it a small quantity of hydrocyanic acid, which is neutralized with caustic soda.

At their outlet the gas shows 75°–80° F. They are conducted into the two cast-iron absorbers  $C_1C_2$ , which are cooled on the outside and which contain caustic alkali. The hydrocyanic acid is absorbed, and the nitrogen dioxide is set free unaltered. This latter gas is brought in contact with air in order to recover the nitric acid, The recovery of this gas is done by passing the gas mixed with an excess of air through two towers of refractory stoneware *M* and *N*, which inclose quartz pebbles, and into which falls a shower of cold water.

The amount of water and the volume of air used in the reaction should be carefully regulated in order to recover an acid of uniform concentration. However, it is necessary to have an excess of air over the theoretical quantity. This excess of air carries a part of the heat liberated by the oxidation of the nitrogen dioxide and serves as a refrigerating agent. The mixture of acid thus recovered, on coming out of the second tower is conducted directly into the first decomposition carboy, where it oxidizes a new quantity of sulphocyanide.

The whole circulation of the gases is made certain by Koerting injectors.

The last operation is the evaporation of the cyanide solution in order to have a commercial product. This procedure is easily accomplished in the laboratory, but quite difficult on an industrial scale. In fact the evaporation of large amounts of cyanide solutions always causes a more or less complete transformation of cyanogen into ammonia. This loss is chiefly due to the action of superheated steam in the cyanide mass. This objection may be easily removed by evaporating the solution in vacuo and by keeping it constantly stirred. The product obtained under these conditions is a white powder more or less agglomerate. It is free of sulphur and therefore particularly suitable in the extraction of gold. It contains, however, several impurities, due mainly to the caustic solutions used. J. T. Conroy, who has made a thorough study of

Raschen's process,\* states that the precautions taken in order to avoid any liberation of such toxic gases as hydrocyanic acid and nitrogen dioxide are perfect, and the total absence of any odor in the works is a convincing proof.

**Beringer's Process.**—Having studied thoroughly the conversion of sulphocyanides into cyanides by the oxidation process, Beringer discovered that the formation of carbonic acid was due to the presence of free mineral acids, and thereupon conceived a process whose object is to carry on the reaction in such a manner as to form no free acid, or at least if any be formed, its effect is not perceptible.

In order to do this he uses nitric acid in sufficient quantity, but in the form of nitrate (of calcium or of barium). By causing a mineral acid, which is capable of setting free nitric acid from the nitrate, to act upon this salt, the nitric acid will act on the sulphocyanide as an oxidizing agent; sulphuric acid will be formed at the same time as the oxidation is produced, but this acid will liberate a fresh quantity of nitric acid, which will oxidize more sulphocyanide, while the sulphuric acid formed will be held by the base of the sulphocyanide according to the reaction



In this way Beringer claims that the carbonic acid formed at the expense of hydrocyanic acid is reduced to a minimum, and that the yield of this latter is almost theoretical.

The operation takes place in a hermetically closed receiver provided with stirrers. Into this receiver 32 kg. of barium nitrate and 700 liters of water are placed and the temperature brought to the boiling-point. Then are added slowly, either separately or mixed together in portions about equal, 37.2 kg. barium sulphocyanide and 31.6 kg. sulphuric acid of sp. gr. 1.84, to each of which 100 liters of water have been added.

The hydrocyanic acid liberated is carried away by the watery vapor and absorbed in suitable receptacles.

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\*Jr. Soc. Chem. Ind., 1899, May 31.

## II. REDUCTION PROCESSES.

The oxidation processes have never been employed industrially to any great extent. Rauschen's methods only have enjoyed some interesting developments. They are in themselves rather dangerous, for they all set prussic acid free, an excessively poisonous gas. Moreover, there is always fear of a later oxidations, the result of which would be a greater or less loss of cyanogen.

The reduction processes are much more numerous, practical, and profitable, and at the same time free from danger. They are the only ones susceptible of being used in the industry of the cyanides obtained by the conversion of sulphocyanides.

The various substances proposed for the accomplishment of the reduction are quite numerous: Hydrogen, carbon, hydrocarbons, various metals, etc.

**Playfair's Process.**—Playfair has thoroughly investigated along this line, and his remarkable researches have served as a basis for the reduction processes which are used at the present time.

In one of his earlier investigations Playfair attempted to heat to redness a mixture of sulphocyanide of sodium or of potassium in a current of hydrogen, based on the following reaction:



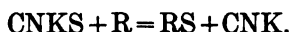
He noticed an abundant liberation of hydrogen sulphide; after the reaction was completed there remained in the combustion-tube a mixture of sulphide and cyanide in almost equal proportions; from his data, only about 80% of the sulphocyanide was decomposed. In the above equation, 110 parts of potassium sulphide corresponding to 130 parts potassium cyanide, the product of the reaction yielded 20% less cyanide than the theoretical amount. Besides, one half of the cyanogen is lost, as it is set free in the form of nitrogen, and the separation of the cyanide from the sulphide is not a very easy matter. This process was therefore quite impracticable. Several years later Conroy repeated Playfair's experiments and confirmed every result.

Next, Playfair tried the use of hydrocarbon vapors—naphtha vapors for example—as reducing agent. As in the preceding experiment he noted an abundant liberation of hydrogen sulphide, but at the end of the reaction he found no traces of cyanides. The residue

was composed entirely of sulphides together with slight traces of formates.

When he heated sulphocyanide of sodium with charcoal, he obtained no better results. In this case he obtained traces only of cyanide and a considerable quantity of sulphide.

Then Playfair tried the use of metals—at first lead and zinc, for these only appeared suitable. The metals decomposed the sulphocyanide either in fusion or in solution according to the reaction



After many experiments, Playfair adopted the following procedure:

He used a receiver made of black lead, whose form is that of an inverted muffle and which is provided with a tightly fitting lid. This apparatus is placed in a furnace in such a way that the top of the receiver extends 2 to 5 centimeters above the upper border of the furnace so that it becomes heated only at the bottom and the sides. Zinc is then melted in the presence of a small quantity of pulverized charcoal, which maintains a reducing atmosphere in the crucible. When the zinc is completely fused dry sulphocyanide is added, either cold or even in a melted state. The mass is kept stirred and the reaction continued till the mass becomes quite thick and begins to redden. At this point the reaction is complete. The mass is then allowed to cool, protected from the air. When cold, the mass is easily removed from the crucible, which does not appear at all attacked. The color of the mass should be pearly gray, if the reaction has been successful, in which case its solution will be entirely free of soluble sulphides. But if the mass has been superheated, which happens especially when too large crucibles are used, it has a brownish and sometimes even a reddish color, and the solution may contain as much as 15% of alkaline sulphide.

As a rule one must assume a loss of about 5%, due partly to moisture and partly to the formation of small quantities of cyanate and carbonate. One should add also to the above loss that which may result from the formation of the double cyanide of zinc and potassium or sodium in consequence of a too high temperature, but this loss may be easily avoided by the use of a slight excess of sulphocyanide.

The melted mass is subjected to a systematic lixiviation in a series of vats. The alkaline cyanide solution is separated from the insoluble zinc sulphide by decantation. This latter substance constitutes about 65% of the fused mass. The solutions thus obtained vary considerably in concentration; that is, from 4 grams of sodium cyanide per liter to 220-240 grams. These latter solutions are evaporated in vacuum to the consistency of a thick paste, which on cooling crystallize. The following is an analysis, made by Playfair, of one of these solutions. The figures represent the amounts per 100 cc. of solution to be evaporated.

Sodium cyanide. ....	22.00 gm.
Cyanate. ....	3.06
Double cyanide of zinc and sodium. ....	1.55
Sodium carbonate. ....	0.71
Sodium sulphocyanide. ....	1.80

The following is an analysis, made by Playfair, of the concentrated product:

Water. ....	26.00%
Cyanide of sodium. ....	54.70
Cyanate of sodium (contains formate). ....	9.45
Double cyanide of zinc and sodium. ....	3.90
Sulphocyanide of sodium. ....	4.30
Carbonate of sodium. ....	1.65

Playfair's process marks a real progress; it can be applied industrially, since, according to the inventor, the yield is about 70% of the theoretical amount. This result is obtained if care be taken to concentrate the solutions in a vacuum of 66 centimeters, using solutions containing at least 22% of cyanide, so as to avoid loss of cyanogen.

**Dr. Hans Luttke's Process.**—This process is based on the same principle. It consists in melting sulphocyanide with zinc powder. In an iron crucible are fused together

97 kg. sulphocyanide of potassium,  
65 “ zinc powder.

The mass is stirred while being heated, and from the moment it fuses, the crucible is removed from the fire. The reaction then goes on by itself.

When the fused mass is treated with water it yields about .60 kg, of cyanide, i.e., 90% of the theoretical amount. The sulphide of zinc which is obtained as a by-product may be profitably used as a mineral color.

The reaction takes place between  $360^{\circ}$  and  $400^{\circ}$ ; this temperature may be lowered by an addition of 1% to 2% caustic alkali, which at the same time, increases the yield of cyanide.

Various other metals have been tried. Lead, which was also recommended by Playfair, has the advantage of not forming double cyanide of lead and potassium, but on account of its high atomic weight, three times as much lead as zinc are required to perform the same work, while, at the same time, it has a tendency of falling to the bottom of the crucible without remaining mixed with the sulphocyanide.

The reduction of sulphocyanide may be well carried on with the use of tin, but tin sulphide dissolves in rather appreciable quantities in the alkaline cyanide.

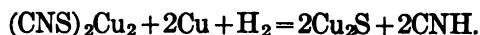
The use of copper is no more successful, for it gives rise to cuprocyanides.

**Process of the British Cyanide Company.**—Notwithstanding the foregoing, this company has quite recently patented a process in which copper is used. This process is based on the fact that when metallic cyanide compounds are heated in a current of hydrogen at a suitable temperature, they set free the whole of their cyanogen in the form of hydrocyanic acid, which may be absorbed by alkaline solutions. The British Cyanides Company, Limited, noticed that the salt which is the best adapted for this reaction is sulphocyanide of copper. This salt, which is first thoroughly dried, is placed in a receiver provided with a stirrer and mixed with finely divided copper in considerable excess (equal quantities of sulphocyanide and of copper). Perfectly dry hydrogen is passed through the apparatus in order to expel the air and then it is heated to  $150^{\circ}$  C., and gradually to  $350^{\circ}$  C.

When the reaction is almost complete, the temperature is raised



to 500° C., the current of hydrogen being constantly kept up. The reaction is as follows:



The gas which is liberated is a mixture of hydrocyanic acid with hydrogen in excess. It is conducted through a strong alkaline solution which absorbs the hydrocyanic acid. The excess of hydrogen may then be collected and used anew. The cuprous sulphide remaining behind may be treated in order to recover the copper or copper salts. In place of hydrogen may be used coal-gas or water-gas provided they be free from carbonic acid, oxygen, and moisture.

Conroy tried using copper and zinc simultaneously, or copper with lead-sodium alloy, but in neither case was he able to obtain a pure product.

The results obtained with iron were quite satisfactory. In his patent, No. 21,451, obtained in 1893, Conroy recommends treating the dry sulphocyanide with finely divided reduced iron, pitch, and a small amount of charcoal in order to prevent oxidation. The reaction takes place at about 400°, but, as Conroy himself noticed it is quite irregular, and the yield may be, in consequence, quite variable. Moreover, it is rather difficult to ascertain exactly the end of the reaction, and if the operation be carried on too far, reactions may take place which are quite opposed to those desired.

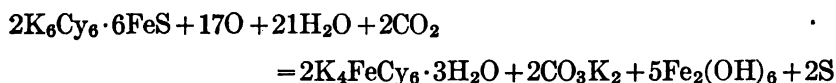
**Hetherington and Musspratt's Process.**—This process (English patent 5830, 1894) is based on this principle: It consists in heating iron filings or turnings with tar in order to reduce the oxide coating to the metallic state. The iron thus treated is mixed in the proportion of 70 to 80 parts with 20 to 40 parts tar and 100 parts alkaline sulphocyanide. This mixture is heated to 350° C., thereabouts, in a closed vessel connected by means of a tube with a retort, where the volatilized sulphocyanide is condensed. The resulting product is iron sulphide, a tar-like residue, and alkaline ferrocyanide. It is treated with hot water, and the filtered solution is subjected to the action of a current of carbonic acid, which displaces the hydrogen sulphide, after which the solution is concentrated to crystallization.

**Process of the Silesia Verein Chemische Fabrik.**—This process is in all points about the same as the foregoing. The sulphocyanide is first melted, then poured upon reduced iron filings, turnings, or shavings, and then heated to dull redness. For this purpose 1 kg. of iron may be profitably used for each kilogram of crystallized sulphocyanide.

If the sulphocyanide be in solution, this is concentrated, and iron shavings added in sufficient quantity to form a pasty mass. This is then transferred to receivers of moderate dimensions which can be transported and heated at a temperature not above 800°. In order to complete the decomposition properly, incandescent bodies, such as pieces of iron, charcoal, and highly heated stones, are thrown on the mass. Then the receiver is removed from the fire and allowed to cool.

In each case the product is treated either with water, in order to obtain ferrocyanide, or with alcohol, in order to obtain cyanide.

**Goerlich and Wichmann's Process.**—This process differs but little. It consists in fusing the sulphocyanide with iron, passing a moist current of air charged with carbonic acid through the fused mass and then treating it with water according to the reaction



At the present time the transformation of sulphocyanides into cyanides is preferably done in the wet way.

These processes originated with the patents taken out by Pitt and Bower, the object of which was the recovery of the cyanide compounds occurring in gas-liquor.

**Bower's Process.**—In Bower's first process these gas-liquors are treated with addition of metallic iron or ferric salt in sufficient quantity to convert the whole of the cyanide compounds into ferrocyanide and iron sulphocyanide. After distilling off the ammonia in the presence of lime, the residual liquors containing the sulphocyanide and ferrocyanide of calcium are treated with an acid solution of cuprous chloride, which precipitates the cyanide compounds as insoluble cuprous salt. While this precipitate is still moist, it is treated with finely divided iron in order to convert it into soluble

iron sulphocyanide and insoluble iron ferrocyanide. At the same time metallic copper is formed. The ferrocyanide of iron, which is separated by filtration, is treated with a strong alkaline solution in order to obtain an alkali ferrocyanide. The solution of iron sulphocyanide is evaporated.

Later Bower noted that when the decomposition of copper sulphocyanide is brought about by the use of iron at a high temperature and under pressure, the copper which is set free reacts with the sulphur of the iron sulphocyanide and forms copper sulphide and iron ferrocyanide. Bower immediately obtained a new patent, according to which the iron sulphocyanide obtained as before stated is treated with metallic copper in an autoclave and at a high temperature under pressure.

The reaction follows:



The precipitate obtained is afterward treated with an alkaline or alkaline-earth solution giving a soluble ferrocyanide.

**Conroy's Process.**—Taking up Bower's work, Conroy thought of substituting another and less expensive metal for copper, and chose iron. He noted that if a solution of iron sulphocyanide be boiled under pressure with metallic iron there will be formed at

	Undecomposed Iron Sulphocyanide.	Ferrocyanide Obtained.
115°-125° (after heating 13 hours) . . . . .	62.0%	36.8%
150°-165°    "    "    4    "    . . . . .	10.6%	88.0%
190°-200°    "    "    2½    "    . . . . .	9.2%	90.5%

Having settled this important point, Conroy sought to obtain a similar result with potassium sulphocyanide or other impure sulphocyanide.

His first experiment along this line was with a mixture of potassium sulphocyanide with a soluble iron salt. The results were as follows:

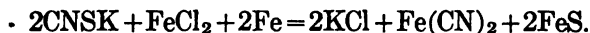
	Non-decomposed Sulphocyanide.	Ferrocyanide Obtained.
At 160° with 1 hour's heating . . . . .	38.0%	52.6%
At 160°    "    2 hours'    "    . . . . .	22.0%	67.5%
At 150°-160° with 5½ hours' heating . . . . .	—	95.0%

The result being favorable, Conroy determined to apply this method on an industrial scale, and in order to do this he undertook, in company with Hawliczek and Clayton, experiments bearing upon calcium sulphocyanide, the important industrial waste product in the manufacture of gas.

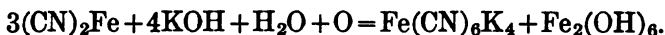
In a cast-iron cylindrical autoclave provided with a stirrer turning at the rate of 40 revolutions per minute a mixture of (1) a solution of calcium sulphocyanide, 400 g. per liter; (2) a solution of ferrous chloride, 250 gm. per liter and an excess of iron filings or shavings is heated to 135°-140° C. and under a pressure of 50-60 pounds per square inch. Under these conditions he observed that the time of the decomposition of the sulphocyanide that it varies with the amount and fineness of the iron used, according to the following table

	Iron in Excess of Theoretical Amt.	Sulphocyanide Decomposed.	Time of Reaction.
Iron shavings. . . . .	8 times	92.5%	12 hours
Reduced iron. . . . .	{ 5.55 "	94.0%	5½ "
	{ 1.70 "	85-99	5½ "

According to Conroy the reaction is as follows:

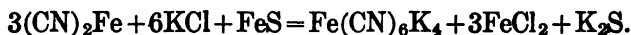


The mixture of sulphide and of ferrocyanide of iron is then treated with a strong alkaline solution, there being formed soluble alkali ferrocyanide, while the sulphide of iron undecomposed remains insoluble:



But this treatment requires a large excess of alkali, and moreover there is an appreciable loss of this compound varying from 12%-28%. It is better to replace it by treatment with hydrochloric acid. In fact, if the mixture be treated with this acid the sulphide of iron goes into solution, while a pale-blue precipitate is formed which is insoluble in hot potassium carbonate, but which yields potassium ferrocyanide under the action of a current of air.

This method presents, moreover, the great advantage of giving ferrous chloride, which may thus be used in the reaction



All these processes yield ferrocyanide, which product must then be reduced to cyanide. They therefore do not solve the problem completely, which is the production of the cyanide direct.

**Raschen, Davidson, and Brock's Process.**—Nevertheless there exist special processes which fulfill this purpose, among them may be cited that of Raschen, Davidson, and Brock (1894). It is based on the conversion of sulphocyanides into cyanides by ignition in the presence of an excess of alkali or of alkaline earth, together with charcoal or a hydrocarbon. The sulphocyanide used in this case is produced by the action of carbonic acid on a mixture of milk of lime, sulphide of carbon, and ammonia heated in a closed vessel. The resulting product is treated with an alkaline carbonate filtered and evaporated to dryness. Quicklime is added to the crude sulphocyanide together with a mixture of powdered charcoal, resin, tar, or any other such substance. The whole mass is heated as rapidly as possible to a bright-redness in a vessel provided with a stirrer.

The mass is then allowed to cool, avoiding as far as possible the access of air, and then it is washed with water. In this way is obtained a solution of alkali cyanide containing a small amount of calcium sulphide, which latter product may be gotten rid of by well-known methods.

Theoretically, this process seems very simple and reasonable, but unfortunately no data could be obtained concerning the yields which it furnishes and concerning its industrial application.

**Etard's Process.**—This process, which has already been mentioned (Chapter I, § 1) and which consists in treating the alkali sulphocyanide with the ferrocyanide of the same metal either alone or mixed with a carbonate, has not, to our knowledge, been industrially applied.

**Finlay's Process.**—Finally may be mentioned the original process, patented in Germany by Finlay (patent 8604, 1896). It consists in producing simultaneously sulphocyanide and alkali cyanide by igniting at  $1000^{\circ}$  a mixture of alkali or of alkaline earth with charcoal in an atmosphere free from oxygen and consisting chiefly of nitrogen and sulphuric anhydride. Through the solution of the mixture thus produced a current of nitrogen and carbonic acid, in the presence of an oxidizing agent, is passed. Hydrocyanic acid

is removed and passes into an alkaline solution, forming an alkali cyanide.

Finlay recommends the following:

A mixture of equal parts of charcoal and caustic or carbonated alkali, especially barium carbonate, is heated to about  $1000^{\circ}$ . A mixture of nitrogen and sulphur dioxide obtained by direct combustion of sulphur in air is transmitted upon the incandescent mass. Under these conditions there is produced a mixture of cyanide and sulphocyanide of barium. When this reaction is complete, the mass is allowed to cool and is taken up with water. After a suitable addition of an oxidizing agent (of the nature and use of which Finlay gives no information) a mixture of nitrogen and carbonic acid obtained by the combustion of charcoal in a current of air is transmitted into this boiling solution. The barium separates out as an insoluble carbonate, while the hydrocyanic acid which is displaced is carried off by the gaseous current. The hydrocyanic acid is condensed in a cooler kept at a temperature of  $4^{\circ}$ – $5^{\circ}$  C. and combined with a caustic alkali. At the same time the sulphocyanide is decomposed into hydrocyanic acid and sulphur dioxide. This latter, carried off by the nitrogen, regenerates thus the initial mixture of gas used for the production of cyanide and sulphocyanide.

On account of its originality, this process deserves some attention, but unfortunately it is quite probable that the liberation of hydrocyanic acid will check its industrial development, as is the case in all those processes where such a liberation takes place.

## II. SYNTHETIC PROCESSES.

### GENERAL REMARKS.

It is the custom to designate under "synthetic or direct processes," all those processes the essential principle of which consists in uniting by means of any energy the three fundamental bodies entering into the composition of cyanides—carbon, nitrogen, and alkali metal—these three bodies capable of being either in a free or nascent state or in a combined state.

The indirect processes which have just been reviewed have been able to supply the needs of the trade at a time when the use of cyanides was very limited, but soon the requirements of industry made necessary simpler, less defective, and less expensive processes.

Nitrogenous organic substances, which for a long time have been the raw materials of this industry, have in general a very high value relatively, because of their extensive use either in human or animal nutrition, or in agriculture, or in other industries. Therefore they could not be economically used for a preparation which utilizes only their carbon and nitrogen.

It is consequently necessary, if it is desired to work under really economic conditions, to make use of waste or refuse products, which are necessarily insufficient, especially from the point of view of the percentage of useful products which they contain.

The percentage of nitrogen in these substances is especially small in comparison with that of carbon; therefore it is always necessary to ignite them beforehand, in order to obtain a much richer nitrogenous charcoal. In this preliminary operation  $\frac{3}{4}$  of the nitrogen is lost under the form of ammonia. This loss is unfortunately not the only one, and at the time of the forming of the cyanide with the nitrogenous charcoal  $\frac{1}{4}$  and even  $\frac{1}{2}$  of that remaining is lost, so that finally only  $\frac{1}{8}$  or  $\frac{1}{4}$  of the total nitrogen is utilized.

If to these losses in nitrogen be added those not less important, occasioned by poor yield, from the point of view of the alkali carbonate used, and those produced by the volatilization of the cyanide at the temperature at which it is necessary to work, it is easy to see that such processes are far from giving satisfactory results or being economical, notwithstanding the remarkable improvements which they have undergone.

It is therefore quite natural to have sought to produce cyanides by the synthetic or direct way, which, besides the advantage it possesses of producing the product desired directly, allows this product to be obtained much cheaper and in a state of greater purity. Of the three substances which, in general, constitute the cyanides, carbon occurs wide-spread, is easily found, and very cheap; the alkali metals are likewise widely distributed. As to the nitrogen, although it occurs distributed in extensive amounts on the surface of the globe, it is quite difficult to produce in a free state.

Constituting four fifths of the atmosphere which surrounds us, it is quite natural to think of utilizing the nitrogen, either in the form of air or in the free state extracted from the air. The idea of using

the atmospheric air in the manufacture of cyanides is not new. It proceeds from a series of observations made by many investigators.

In 1828 a chemist of Besançon, named Desfosses, repeating the old experiments of Scheele and Curandean, remarked that the nitrogen unites with carbon in order to form cyanogen when a current of this gas or of air passes over a mixture of charcoal and carbonate of potash at a red heat.

In 1835 Dawes discovered the existence of cyanide of potassium in the molten masses which are formed in the furnaces for the smelting of iron.

In 1837 the English investigator Clark made the same discovery. In examining an efflorescence which was produced at the orifice of some blast-furnaces on the Clyde, he noticed that it was made up almost entirely of potassium cyanide.

In the same year, having established hot-air bellows in blast-furnaces, Neilson likewise observed the formation of masses which contained up to 43% potassium cyanide.

These were confirmed by other observations, notably in the Harz, at Magdesprung, and at Zuicken by Bromeis in 1842. In 1843 Redtenbacher proved a similar phenomenon in the furnaces at Mariazell in Styria, where the production of potassium cyanide thereby became industrially important.

Moreover, in 1839 Lewis Thompson demonstrated that if a mixture of coke, potassium carbonate, and iron filings be heated at a high temperature and a current of air be passed over the mass, there will be formed potassium cyanide the yield of which will be greater than that obtained by not using air even when animal charcoal rich in nitrogen be used. On account of this remarkable investigation the Society of Arts bestowed a gold medal on Lewis Thompson.

In 1841 Fownser, and likewise Young, confirmed this result.

But other chemists, and particularly Erdmann and Marchand in 1841, and Wöhler somewhat later, disputed their assertions, and claimed that the cyanide formed was due entirely to the nitrogen of the coal and that the reaction would not take place with dry substances.

In 1845 the question of the formation of cyanide in the blast-



furnaces being studied more thoroughly, Bunsen and Playfair were able to show that this product is formed in the zone situated exactly above the blast-pipes through which hot air was being blown. They experimented on this subject with the result that it received scientific and industrial sanction and exerted a considerable influence on the ideas concerning the rôle played by nitrogen. By making an opening in the wall of a blast-furnace of the iron-works at Alfreton, exactly above the orifice of the blast-pipes, they noted the formation of an abundant sublimation of potassium cyanide, which, according to their calculation, might react 188 kg. in 24 hours. From this experiment they drew the conclusion that the cyanide formed was due solely to the atmospheric nitrogen, and not to that chemically combined with the coal. Moreover, they established clearly the probability of this theory by another experiment.

In passing air through a tube containnig a mixture of 1 part sugar charcoal and 2 parts of perfectly pure carbonate of potash, heated to a temperature high enough to cause the reduction of the alkali carbonate, they obtained an abundant formation of potassium cyanide.

In 1851 Riecken confirmed in all points the data presented by Bunsen. This investigator showed without any doubt that cyanogen may be formed in the absence of every other source of nitrogen except that of atmospheric air, provided that the latter be previously heated and transmitted in the form of a continuous current, and that the reaction be carried on at a temperature sufficiently high to reduce the potassium compounds employed to the metallic state.

Some time later Delbruck's new experiments removed all doubt from the works of Bunsen and Riecken.

These first principles being admitted, it was immediately planned to make it the basis of a process for the manufacture of cyanide on an industrial scale.

The first practical application undertaken along this line was in 1843. This was made by Possoz and Boissière, at first in their works at Grenelle, and the next year at Newcastle, under the direction of an English company. This process was based on the fact demonstrated by Desfosses in 1841, that if a current of nitrogen be passed over a mixture of charcoal and potassium carbonate

heated to redness, there is formation of potassium cyanide. Notwithstanding unheard-of efforts, great sacrifices, and several years of struggle and in spite of their rare perseverance, the two French chemists could not hold out against competition, and were forced to abandon the exploitation of their process. That was because the yield of cyanide was small, and consequently the net cost was greatly increased.

Numerous attempts followed that of Possoz and Boissière, and among them may be cited:

*In England*, those of Newton in 1843, Swindel in 1844, Blairs and Bromwell in 1847.

*In Germany*, those of Welden in 1879, and Alder in 1881.

*In America*, those of Mond in 1882, Fogarty in 1883 and 1887, and Dickson in 1887.

*And, finally, in France*, those of Ertel in 1846, Armengaud in 1847, and Margueritte and Sourdeval in 1862.

All these processes are based on the action of atmospheric air on a mixture of charcoal and an oxide or carbonate of an alkali heated to a very high temperature.

The results obtained by these various manufacturers, however encouraging they may have been, were nevertheless far from being satisfactory. Therefore these processes had a very short existence.

The quantities of cyanides produced were, in fact, very small, and the net cost was consequently very great. If to this great objection be added that none the less serious of the rapid wear and tear of apparatus brought about by the extremely high temperature necessary for producing the reaction, the causes of the failure of these attempts will be readily understood.

The attempt was made to overcome the difficulty by utilizing nitrogen in another form, and for this purpose ammonia-gas was suggested. This gas in fact, besides being relatively cheap, is  $\frac{14}{17}$  of its weight in the form of nitrogen, and it has a greater chemical affinity than that of nitrogen. In fact it was proved by the experiments of Langlois and Kuhlmann that if dry ammonia-gas be passed over charcoal heated to redness there will be formed ammonium cyanide according to the reaction



This was not, indeed, a new idea. Brunnquell, later Karmrodt, and finally Lucas had already tried to utilize the ammonia produced in the ignition of nitrogenous organic matters, and which forms part of the volatile products arising from this decomposition. Toward this end these products were made to pass through retorts or cylinders charged with charcoal impregnated with potash; but notwithstanding certain advantages these processes never received industrial sanction.

Laming, in 1843 and 1845, made this idea the basis of two processes for the manufacture of cyanides. But these attempts were likewise futile. Other manufacturers and investigators studied this question also, their results often being contradictory and their experiments were never taken up outside the laboratory.

The weak points of the experiments undertaken along this line are (1) the difficulty of manipulating such a volatile gas as ammonia, (2) the necessity of producing a very high temperature, (3) the considerable loss due to volatilization, and (4) the rapid deterioration of the apparatus.

To the above should likewise be added the fact that at such high temperatures ammonia-gas begins to undergo an appreciable decomposition, which, of course, is lost to the reaction.

Another very ingenious solution of the problem had been proposed by Gelis, and was taken up about 25 years ago by Tcherniac and Gunzburg. It consisted in producing cyanides through the intermediary of sulphocyanides, formed by the action of ammonia on the sulphide of carbon.

During the last few years this question has again become the object of numerous and important researches, but along other lines, and which permits the discovery of a real synthetic process to be foreseen in the near future, a process at once practical and of industrial value.

These processes are based on the action of nitrogen or of ammonia upon the alkali metals or their carbides.

The reaction of ammonia on the alkali metals was shown a long while ago by Gay-Lussac and Thénard.

It is, in fact, known that if perfectly dry ammonia-gas be passed over potassium or sodium at a suitable temperature (not very high) a clearly defined compound, an alkali amide, is obtained which in

contact with charcoal under suitable condition forms alkali cyanide. The low price and the facility with which large quantities of alkali metals are prepared leads to the belief that processes based upon this reaction will be put to practical use. It is evident that in this case it is no longer necessary to produce the extreme temperature required for the reaction of alkaline compounds formerly used, and from this fact losses through volatilization will be avoided while decreasing the wear and tear of the apparatus.

On the other hand, it is to-day clearly proven that carbides are capable of fixing nitrogen, and, under certain conditions, of forming cyanides.

These two important observations have formed the basis of numerous patents recently granted, especially in Germany. The experiments seem to be successful, and in the near future the solution of this question may be met.

The solution would all the more be hastened through the discovery of a practical and economical process of fixing the nitrogen of the air, a question which has likewise made considerable progress, and all the more through the synthetic production of ammonia by the aid of this same nitrogen.

Whenever this problem is solved, that of the manufacture of cyanides will be near its solution.

The synthetic processes put into operation may be divided into two large classes:

- (1) Processes using atmospheric nitrogen.
- (2) Processes using ammoniacal nitrogen.

Some of these processes are capable of using either atmospheric nitrogen or the nitrogen of ammonia. Such processes will only be mentioned in the first class, but will be discussed among those processes which are based on the use of ammonia.

#### A. PROCESSES USING ATMOSPHERIC NITROGEN.

The discovery of potassium cyanide in blast-furnaces, and the remarkable investigations of Bunsen, Playfair, Riecken, and of Delbrück, which fixed in an irrefutable manner the remarkable rôle played by atmospheric nitrogen in this formation, had the happy

result of inciting manufacturers and investigators to utilize atmospheric air, or the nitrogen contained therein for the manufacture of cyanide compounds.

As is well known, the atmosphere is composed of a mixture of oxygen and nitrogen, contaminated more or less, according to circumstances, with water, carbonic acid, ammonia, etc. In reality nitrogen forms about four fifths of the air, since air is composed of 21% oxygen and 79% nitrogen by volume, or 23% and 77% by weight. Air therefore is an inexhaustible and profitable source of nitrogen for the manufacture of cyanides.

At first it was attempted to use the atmospheric air, but the presence of the oxygen interfered considerably with the reactions. That is the reason why the attempt was made to use the nitrogen from which the oxygen had previously been removed.

The separation of these two gases is not such an easy task as one would be led to believe, and several methods have been devised for this purpose. Therefore it may not be out of place, before taking up the study of processes for the manufacture of cyanides by the use of nitrogen of the air, to first pass in review the various means employed for the separation of these two principal constituents of air, oxygen, and nitrogen.

These methods almost all depend on the following principle: If a current of air be passed over an easily oxidizable substance under suitable conditions, this substance will absorb the oxygen and leave the nitrogen free and pure.

Most of the metals, and even certain metalloids—e.g., phosphorus or charcoal—may be used for this purpose.

As a rule, whenever it is desired to obtain almost chemically pure nitrogen, copper or iron is used.

A current of air is passed over copper heated to redness, which absorbs the oxygen with formation of oxide of copper, while the nitrogen is left almost pure. Often passing the gas only once over the metal is not enough for the total absorption of the oxygen. This is an objection which may be easily remedied, and thus a gas absolutely free from oxygen obtained. This operation being carried on at a high temperature, the resulting gases are likewise hot, which fact may be of great use in certain processes.

Lupton has modified this process in such a way that a better

yield of nitrogen is obtained, and the process is carried on continuously.

His process consists in passing air through an aqueous solution of ammonia before passing it over the copper; the ammonia carried away by displacement then passes over the oxide of copper formed and reduces it to metallic copper according to the reaction  $3\text{CuO} + 2\text{NH}_3 = 3\text{Cu} + 3\text{H}_2\text{O} + 2\text{N}$ , thus giving a new quantity of nitrogen.

The copper thus reduced is again oxidized by the oxygen of the air setting the nitrogen free; these two reactions really take place simultaneously. The gases obtained contained greater or lesser quantities of ammonia and aqueous vapor, which may be easily gotten rid of by suitable means.

The chief objection to these processes is the use of copper, which is an expensive metal, even in Lupton's process, where it is recovered, for it finally undergoes physical modifications, becoming brittle and falling to pieces, which prevents its being suitable for further use.

The process of obtaining nitrogen by the combustion of charcoal in a current of air has the objection of yielding an impure gas, always contaminated with carbonic oxide, and even with a small amount of oxygen.

In these various processes the oxygen is lost, as may be easily shown. It would therefore be of advantage to extract these two gases simultaneously from the atmosphere, i.e. to utilize the residue from the preparation of oxygen, a residue which consists entirely of nitrogen.

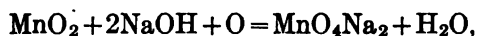
The same remark may be made concerning the utilization of the residual gases of the new industry—the manufacture of peroxide of sodium. This product is obtained by passing a current of dry and pure air over heated sodium, the gaseous residue consisting chiefly of nitrogen.

Any of the methods for the production of oxygen from air may be utilized, among which may be mentioned those of Boussingault, Tessié du Mothay and Maréchal, Mallet, etc.

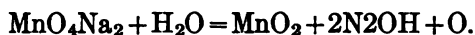
Boussingault's process consists in fixing the oxygen by means of baryta, there being formed barium dioxide, which under the action

of heat and reduced pressure yields one molecule of oxygen, with the re-formation of baryta. If care be taken to add certain substances so as to prevent fritting, the baryta may be used almost indefinitely. This process has the advantage of being rapid, since each operation for the complete oxidation and deoxidation lasts 10 minutes, and 140 may be made per day.

The process of Tessié du Mothay and Maréchal utilizes a mixture of manganese dioxide and caustic soda. When this mixture is subjected to a red heat in a current of air, there is formed sodium manganate,

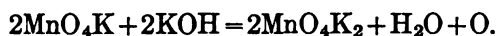


which, when heated with superheated steam at  $450^\circ$ , liberates oxygen and yields anew the original substances,



The process which was brought out in 1897 by Etard is quite similar to the above, in that it also utilizes the oxygen salts of manganese for the absorption of oxygen; but, as Etard himself says, his process does not consist of a simple chemical cycle: it is based upon a state of equilibrium.

If potassium permanganate be subjected to the action of a boiling alkali, there is produced, under the definite conditions of pressure and temperature, a liberation of oxygen,



The reaction is, moreover, a reversible one, and if the conditions of temperature and pressure are changed, the manganate absorbs oxygen of the air and yields again the permanganate. The nitrogen set free may be collected by means of suitable apparatus. On account of the separation of the oxygen and the nitrogen, this process should be tried on an industrial scale.

As early as 1892, Parkinson installed a similar process in Manchester, which produced 42 cubic meters of oxygen in 24 hours. He uses a mixture of kaolin and permanganate, which is heated in retorts at a reduced pressure, and even in vacuum. Under these conditions the permanganate yields its oxygen. It reabsorbs oxygen when heated to  $550^\circ\text{C}$ . under pressure in a current of compressed and hot air. There are five retorts, one of which is used

for reheating the air. This air is compressed by means of a pump in a compressor, whence it is driven to the retorts arranged in such a manner that one of them absorbs the oxygen while the other liberates it. The nitrogen is continually removed by means of a sniffing-valve, and the separation of the two gases is automatically regulated by means of a system of valves. The permanganate mixture is very stable, since it is altered neither by moist air nor by carbonic acid.

Numerous patents have been taken out in regard to the manufacture of oxygen, but they are only more or less successful modifications of the processes brought out by Boussingault and Tessié du Mothay.

Mallet's process, which is likewise much to be recommended, consists in using a 20% solution of cuprous chloride. This solution is placed in a retort, which is heated to 100°, and a rapid current of air is passed through. The cuprous chloride is converted into the oxychloride, which, when heated in the same retort to dull redness, loses its oxygen and becomes reconverted into the cuprous chloride.

Several years ago other rather ingenious processes were shown. They are based not upon chemical reactions, but upon purely physical phenomena, especially those of dialysis and solubility.

In the first case the processes are based upon the differences existing between the rate of dialysis of nitrogen and oxygen. Of such is Villepigne's process, patented in 1896. This consists in causing air to pass through a series of membranes made of caoutchouc, through which the nitrogen traverses less rapidly than does the oxygen, so that at the last membrane the oxygen emerges almost pure, leaving the nitrogen behind in each membranous compartment, which is removed by special means.

It is not known that such processes are successful or that they are employed on an industrial scale. Nevertheless this is not the last to be heard upon this subject, and the future will probably show us what to expect from these new methods.

Finally, another very ingenious process must be mentioned, one which likewise is based upon the difference in the physical properties of nitrogen and oxygen, and which seems to merit an important industrial place. This is the process of Raoul Pictet, who is already well known in the scientific world through his remarkable



researches on the liquefaction of gases. From the "Bulletin de la Société des Ingenieurs civils," before which, on June 7, 1901, Pectet elaborated his new process, the principal features are here extracted so as to give a clear idea of this discovery.

The principle of this method is as follows: The point of liquefaction of oxygen under atmospheric pressure is about  $-183^{\circ}$ , whereas that of nitrogen under the same conditions is  $-195^{\circ}$ . Therefore the nitrogen is sensibly more volatile than the oxygen, and the difference of  $12^{\circ}$  which exists between these two boiling-points differentiates, as the theory of heat shows, at such low temperatures, two liquids such as  $40^{\circ}$  would differentiate at temperatures of  $60^{\circ}$  to  $100^{\circ}$ .

It is therefore easy to see that if a mixture of these two gases, previously liquefied, be vaporized, it will be possible to obtain, on the one hand, pure nitrogen, and, on the other hand, equally pure oxygen, by a process perfectly analogous to that upon which the system of fractional distillation depends. Nevertheless the problem is inverted, from a practical point of view, since it is necessary first to liquefy the two gases and then to vaporize them in order to collect them in the gaseous state.

Thus, the inventor succeeds in separating the two gases on an industrial scale. The air is first suitably dried, then it is compressed into an apparatus completely immersed in liquid air. Under the influence of the temperature and pressure, this air is in its turn liquefied by giving up its latent heat of condensation, under the influence of which an equal quantity of the liquid air of the container becomes vaporized. In this way, with a very slight expense of energy and a definite quantity of liquid air, unlimited quantities of atmospheric nitrogen and oxygen may be set free. Now, the difference existing between the points of liquefaction of these two gases being known, the more volatile nitrogen will escape before the oxygen, and it will therefore be possible to collect them separately by means of suitable apparatus. In this way three classes of gas are obtained:

Nitrogen purer than. ....	90.00%
Oxygen at a purity of.....	50.55%
Oxygen purer than. ....	90.00%

and also carbonic acid, which always exists in air, and which is collected in the solid state.

As will be seen, this is a most ingenious process, practical as well as ingenious, and likewise not at all expensive; qualities which seem to warrant its coming application on an industrial scale.

Having firmly established the theory of the formation of cyanides, and the remarkable rôle which is played by atmospheric nitrogen, it was immediately attempted to turn this discovery to account. At first view, and at least theoretically, nothing seems simpler than to combine the three elements, nitrogen, carbon, and alkali metal; but the experiments undertaken to fix the nitrogen of the air on a practical scale have not always given results which would lead one to expect its fulfillment. Nitrogen has in fact quite definite negative properties, and its fixation is a difficult problem which has not yet been solved satisfactorily, although remarkable progress has been made.

The first attempts to fix nitrogen of the air with a view to the production of cyanides have all completely failed. Not one of them obtained the support of the manufacturer; nevertheless it is extremely interesting to study them, for they are a step toward the truth, and they have had an incalculable bearing on the progress of this industry.

**Bunsen's Process.**—This first process was attempted on an industrial scale in 1845. This was shortly after the efflorescences of potassium cyanide were discovered in the blast-furnaces. Starting from the idea that the potassium cyanide formed was due to the action of air, Bunsen constructed a special blast-furnace for the production of potassium cyanide. Its shape was similar to that of ordinary blast-furnaces. It was filled with superposed layers of charcoal and potassa and heated to a high temperature by the combustion of a portion of the charcoal. At the same time a powerful current of air was blown through the mass by means of an air-exhauster. Under these conditions cyanide of potassium was formed, which flowed through the lower part into a receiver *ad hoc*. The product thus obtained was highly contaminated with such impurities as charcoal, alkaline salts, and mineral salts, due to the ash of the combustible material, and it could be used only in the preparation of yellow prussiate of potash. Besides this serious objection, there were others no less serious, such as the losses through volatilization and the difficulty of conducting such an operation, especially of regu-

lating the temperature and the draft of air, all of which caused the abandonment of this process.

**Possoz and Boissière's Process.**—This process, successively put into operation at Grenelle and at Newcastle, had no better success. The principle is the same as in Bunsen's process, differing from it only in the modification of the apparatus, which allowed the temperature and the intake of air to be regulated. Notwithstanding their patient efforts and an unceasing struggle of several years, these two French chemists were compelled to abandon their project, not being able to meet foreign competition, which sold cyanide at a lower price than theirs. Yet during the first year of their work at Grenelle, in 1843, Possoz and Boissière succeeded in producing 15 tons of an excellent quality of ferrocyanide. But the high cost of fuel and of refractory brick at Paris compelled them to go to England. After completing arrangements with Bramwell and Hughes, they settled at Newcastle-on-Tyne, where, in 1844, their process was established. The process was as follows:

Small pieces of wood charcoal of good quality were saturated with 20 or 30% of caustic potash, or of carbonate of potash moistened with a quantity of water just sufficient to dissolve it. After desiccation, this material was charged into vertical retorts heated on the outside in a furnace at white heat.

The retorts were 3.50 meters long, 0.60 m. outside diameter and 0.492 m. inside diameter. The upper portion was of refractory clay and was 0.23 m. in thickness; the lower part, which served as cooling-chamber for the cyanide formed, was of iron. The height, heated to white heat, was 246 millimeters. A portion of the gases of combustion, quite rich in nitrogen, was heated to a white heat by passing it through a superheater, where it was compressed by means of a pump. On coming out of the superheater, the gases penetrated into the retorts through small lateral slits. After 10 hours' heating and action of the gases, the cyanide mixture was removed automatically and in regulated quantity from the bottom of the retort. This mixture was allowed to fall into a cooling-chamber and thence into vats containing water and sulphate of iron. By means of a similar automatic system a new charge of charcoal and potassa was added and the operation repeated.

Every half hour the apparatus was charged with an amount

equal to 15 kg. wood charcoal containing 25% potash, and a corresponding quantity of cyanided charcoal was removed. The operation was in this way continuous.

In 24 hours each apparatus was charged with 720 kg. dry charcoal-potash containing 460 kg. wood charcoal and 260 kg. carbonate of potash. During the operation the mass decreased one half in volume. It contained from 30 to 50% potassium cyanide. The number of these apparatus was twenty-four, twenty of which were in operation, two ready to be used, and two being repaired. Each one of them produced 50-70 kg. of ferrocyanide per day.

The net cost at the works in Newcastle, in 1846, was 1.86 francs per kilogram, itemized as follows on the basis of 1000 kg. of ferrocyanide of potassium:

7000 kg. wood charcoal, crushed, @2.50 fcs. per 100 kg....	175 fcs.
1000 kg. potash from America @ 50 fcs. per 100 kg .....	500
30 tons coke @ 8 fcs. ....	240
20 tons coal @ 2.50 fcs. ....	50
1 ton carbonate of iron, powdered.....	25
120 men and children (labor).....	375
Maintenance, wear, interest, etc. ....	500
	<hr/>
	1865 fcs.

Possoz and Boissière's process was in operation at Newcastle during the three years 1844 to 1847. The works produced 1 ton of potassium ferrocyanide regularly per day.

That is certainly an appreciable result, but when the process was abandoned, the company could show for this result only a very large deficit, due chiefly to the rapid wear and tear of the apparatus, which it was necessary to repair frequently, and to the losses in carbonates, which amounted to three parts for every one part of prussiate produced. Moreover, the amount of cyanided charcoal to be subjected to lixiviation was far too small in proportion to the amount of ferrocyanide obtained.

Other attempts preceded or followed that of Possoz and Boissière. But, like this one, they also proved fruitless, and not one of them has, to our knowledge, succeeded in giving profitable results.

The yield was too small to produce a cyanide capable of competing successfully. To understand the causes which made these processes abortive, one needs only to consider that in such innovations only 4% of the nitrogen was fixed, that the high temperatures necessary in these processes resulted in rapid wear and tear of the apparatus and in enormous losses through volatilization, and that moreover the product obtained was so impure that it was necessary to purify it at great cost. Yet they deserve to be mentioned.

**Newton's Process.**—First comes Newton's process patented in 1843 in England. In this process the inventor causes the gas coming out of lead chambers to pass over a mixture of charcoal and potash, or of charcoal impregnated with 20–30% carbonate of potash heated to a suitable temperature. The yield was said to be 50% of the theoretical. The process was carried on from 1840–1847, when it was abandoned, the losses in carbonate of potash being enormous and the apparatus deteriorating rapidly. Newton noticed that wood charcoal gave better results than coke, that potash was preferable to soda, that the yield increased with increase of temperature, and that water-vapor exerted a detrimental action. In 1844 Sinndel passed nitrogen over charcoal in closed vessels at a high temperature.

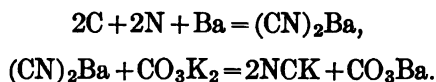
**Blairs' Process.**—Blairs caused nitrogen to be passed over a mixture of carbon and potassa in a shaft-like furnace, which was heated by a grate placed in the exterior casing. The products of cyanide and potash were collected in chambers or in ferric solutions. The residual charcoal was treated with water and furnished a fresh amount of cyanide.

**Armengaud's Process.**—This process (1847) differs from the preceding in that the inventor operated in the presence of water. All these processes, as well as those of Alder (1879) and Weldon (1881), differ from each other only through modifications pertaining to the apparatus, with the object of the introduction of air and the production of heat.

**Margueritte and Sourdeval's Process.**—This process (1862) is the only one which merits more attention. The inventors substituted baryta for potassa for many well-grounded reasons. In fact, baryta is much cheaper than potassa, and is infusible at very high temperatures; moreover, as is well known,

barium fixes nitrogen with great ease. (It would even be ideal to find masses of barium or calcium in order to fix the nitrogen of the air. Lithium has also been mentioned, but it is a rare element and too difficult to prepare.) It attacks the apparatus much less than does potash, and the wear and tear of the vessels is diminished because the temperature necessary for the formation of barium cyanide is much lower than that of potassium cyanide.

This process may be operated in different ways. First a mixture is made consisting of carbonate of barium with 20 to 30 parts of tar, resin, pitch, wood charcoal or coke, which mixture is heated to high temperature under the action of a current of air. Under these conditions the baryta absorbs nitrogen with ease, with formation of barium cyanide, which is converted into alkali cyanide by double decomposition by the reproduction of barium carbonate:



This is one of the rare processes invented along this line which has given good results, and inventors have appeared to be well satisfied with its industrial practicability.

**Mond's Process.**—Margueritte and Sourdeval's process was taken up in America in 1882 by Mond, who modified it somewhat, and who obtained from it good results. Mond used a mixture consisting of charcoal, magnesia, and carbonate or oxide of barium previously ignited out of contact with air.

According to his German patent No. 21175 (1884), he operated as follows:

Briquettes composed of a mixture of witherite (natural carbonate of barium), pulverized wood charcoal or coke, and pitch in the following proportions:

Carbonate of barium .....	32 parts
Wood charcoal.....	8 “
Tar.....	11 “

These briquettes were submitted to the action of a reducing flame in such a manner as to char the pitch and to dissociate the carbonate of barium.

They were then ranged in an annular furnace, where there was directed a current of gas rich in nitrogen and as poor as possible in oxygen, carbonic acid and water-vapor; for example, that which escapes from the carbonic-acid absorption apparatus in the ammonia soda process. This gas was previously heated to a temperature about  $1400^{\circ}$ . In order to do that, it passed through into the first furnace containing briquettes already cyanated, which it cooled while at the same time heating itself. On coming out of this furnace, it passed into a Siemens regenerator, and from there into the furnace where the reaction takes place. When the mass was thought to be sufficiently cyanated, it was drawn out of the furnace, care having first been taken to have the contents of the furnace cooled to about  $300^{\circ}$ . The yield was about 40%.

**Weldon's Process.**—Weldon (1879) made use of a revolving furnace similar to that employed in the manufacture of soda and in which at a dull-red heat he caused nitrogen to act upon a mixture of charcoal and alkali.

**Fogarty's Process.**—To the above must be added the processes patented in America in 1883 and 1887 by Fogarty and Dickson respectively.

Fogarty begins by producing a heating gas highly superheated, and consisting of a mixture of carbon monoxide, hydrogen, and nitrogen. Then he causes this gas to pass into retorts, into which he transmits in the same direction a measured volume of hydrocarbon vapors obtained from the distillation of oils. The mixture of gases comes in contact with a definite quantity of powdered incandescent lime, which falls from the top of the retort. This gas contains, therefore, no oxygen nor carbonic acid and the hydrocarbons are consequently broken up into acetylene, carbon, and hydrogen, which, in contact with lime and nitrogen, produce calcium cyanide.

The reaction may take place in two ways:

(1) Either by the combination of nitrogen and calcium with acetylene at the temperature at which this gas is formed, (2) or by the union of nascent carbon produced by the decomposition of acetylene,  $C_2H_2 = C_2 + H_2$ , with nitrogen and calcium.

The experiments, of Fogarty justify this hypothesis, the most favorable temperature for the reaction being  $2200$  to  $2300^{\circ}$  F.

**Dickson's Processes.**—Dickson injected a mixture of air, water-vapor, and powdered charcoal into a chamber filled with powdered alkali and heated to a proper temperature, naturally quite high. This heat was produced by the combustion of the gases.

**Lambilly's Process.**—Not till 1889, with the appearance of the processes of Lambilly and of Chabrier, have real improvements in the manufacture of cyanides been noted. These two inventors sought first of all to produce ammonia from the nitrogen of the air by passing through cyanides. Their various patents show a deep knowledge of the phenomena of cyanuration.

The first two of these patents were taken out with a view especially toward the production of ammonia through the intermediary of the cyanides. The first one (No. 199977), taken out August 8, 1889, is based on the following well-known facts:

(1) The volatile hydrocarbons are decomposed at a red heat into hydrogen and more condensed carbides.

(2) When nitrogen comes in contact with nascent hydrogen, it unites with it to form ammonia if the temperature is lower than that of the decomposition of this latter body.

(3) The oxides of the alkalis or alkaline earths are reduced in the presence of charcoal and absorb nitrogen in order to form cyanides at temperatures naturally varying with the kind of oxidizing agent used.

The inventors proposed to operate this process on an industrial scale as follows:

The hydrocarbon gas is produced by the distillation of coal, wood, peat, petroleum; the nitrogen is obtained from the atmosphere from which it is extracted by processes already known (those of Tessier du Motay, Boussingault, or Mallet). It is mixed with the carbide gas in amounts varying with the composition of the hydrocarbon. This gaseous mixture passes through a series of cylindrical retorts arranged in one or more furnaces. These retorts are charged with a mixture of charcoal and oxide of alkali or alkaline earth and the whole heated to redness. The inlet of gas is stopped when the amount already taken in is judged to be sufficient to convert the contents of the retorts into cyanide. Under these conditions the hydrocarbon gas is broken up. Its decomposition goes on



and is completed at the temperature at which it begins, if care be taken to remove the gases formed from the atmosphere in contact with the substance undergoing dissociation, in such a manner that the pressure is always less than the tension of dissociation. This condition is found fulfilled; in fact, the formation of ammonia by the union of nascent hydrogen and nitrogen takes place with contraction. There is thus produced a partial vacuum which, together with the carrying away of the ammonia, causes a pressure inferior to the tension of dissociation. The carbon of the carbide, being in the nascent state in the presence of nitrogen and of substances capable of becoming converted into cyanides, yields this latter body. According to the inventors, if the conditions of temperature and pressure are fulfilled, it is possible to fix an amount of nitrogen corresponding theoretically to the hydrogen and to the carbon of the carbides used.

An ingenious modification of the above process is that brought out by Lambilly and Chabrier in the second patent (No. 202700), of December 21, 1889. It consists in removing the hydrogen from the mixture of hydrocarbons and nitrogen before its entrance into the cylinder where the conversion into cyanide is to take place, and for the following reasons:

Illuminating-gas is composed of methane and ethylene, which are broken up at red heat into hydrogen and acetylene. In the presence of nitrogen and of bodies which may be converted into cyanides, acetylene gives rise to these latter, but the hydrogen set free with acetylene through the decomposition of the hydrocarbon places, because of its tendency to recombine with the acetylene, a serious obstacle in the way of the formation of cyanogen, which therefore takes place but slowly. It is therefore necessary to rapidly remove this hydrogen, by combining it with nitrogen under the form of ammonia, before the appearance of the mixture of acetylene and nitrogen into the cylinder where the cyaniding is to take place. For this purpose the gas first passes through a cylinder containing oxide of copper, obtained from the process of extracting atmospheric nitrogen by the use of this metal. It reduces the oxide of copper and thus forms anew the metal, which may be used in the preparation of fresh quantities of nitrogen. The hydrogen being eliminated by this means, the gaseous mixture, which consists now

of only acetylene and nitrogen, passes into the second cylinder containing the substances to be converted into cyanide. The flowing and the outlay of gas and of nitrogen are regulated through the result of the combinations. The inventors claim that in this way a minimum of 1 cubic meter of nitrogen may be fixed; that is, 1.25 kg. per cubic meter of illuminating-gas used.

In his patent No. 210365 of December 20, 1890, Lambilly seeks only the production of cyanides. This patent is extremely interesting, its chief object being to produce nascent carbon, which renders its union with nitrogen all the easier.

It still depends on the decomposition of illuminating-gas in an atmosphere of nitrogen and in the presence of substances capable of being converted into cyanides. But the decomposition of the gas is carried on under certain conditions which permits a gas extremely rich in acetylene ( $C_2H_2$ ) to be obtained, which is finally resolved into its elements. In order to carry on this dissociation, the inventor starts from the consideration that illuminating-gas is a mixture varying more or less, according to its method of preparation, in the amounts of hydrogen (a gas containing the least possible amount of this element should be prepared), and the three hydrocarbons, ethylene, methane, and acetylene, and that these three bodies are decomposable at different temperatures. In fact, acetylene is broken up into its elements only in the neighborhood of a white heat, while at a red heat ethylene breaks up into acetylene and hydrogen, or methane and hydrogen, or a mixture of these three gases according to the degree of redness and the time to which it is subjected to this temperature. Methane is decomposed at a like low temperature into acetylene and hydrogen. From these facts the inventor concluded that if care be taken at the beginning to limit the action of the temperature, only the ethylene and methane will be decomposed, forming a mixture very rich in acetylene, which will combine with the acetylene already existing normally in the gas. Then by raising the temperature to a white heat, the acetylene will in its turn be dissociated into its elements.

The manufacture of cyanides by this method will therefore comprise four phases:

- (1) The preparation of nitrogen.

- (2) The preparation of illuminating-gas.
- (3) The dehydrogenation, or, better, the carbureting of the latter.
- (4) The conversion into cyanides.

The nitrogen is prepared as in the previous method, by passing air over copper heated to dull redness. The gas is prepared by the usual methods, then freed from its hydrogen by passing it over copper oxid produced in the preparation of nitrogen. The mixture which is to be converted into cyanide is composed of charcoal and oxids or carbonates of the alkalis or of barium finely powdered. This is placed in cylindrical retorts and heated to a high temperature, which should not, however, reach a white heat.

Right here Lambilly improved the methods of his predecessors in two important particulars viz., in the use of the materials for manufacturing cyanides. Having noticed that when the alkali and charcoal are heated there is formed a considerable amount of carbon monoxid, which prevents the intimate contact of the substances which are to be converted into cyanide with the current of nitrogenized and carbonized gas, he avoids the passing of this gas just as soon as the temperature is favorable for the formation of cyanides, and removes the carbon monoxid as fast as it is formed. For this purpose he makes use of the principle established by Sainte-Claire Deville, that the dissociation of a body continues and ends at the temperature at which it begins provided care be taken to remove the products of dissociation. In this way Lambilly economizes fuel, for the dissociation of the alkali oxid takes place at a relatively moderate temperature, and, moreover, he uses the carbon monoxid in heating the furnaces in which the cyaniding process proceeds. From the moment carbon monoxid ceases to be formed, he allows the mixture of gas and nitrogen to pass.

The second improvement quite naturally follows from the first.

In fact, being no longer troubled by carbon monoxid, the mixture of gas and nitrogen may be allowed to come under pressure into the cylinder where the cyaniding process goes on, by giving to the hydrogen, which is the residue of the reaction, but a limited outlet. In this way a more intimate contact of the substances to be converted into cyanides with the reacting gases is obtained.

In order to hasten the decomposition of the carbides and the formation of the cyanides, Lambilly proposes, moreover, to add to the mixture of charcoal and alkali a certain proportion of small pieces of nickel, iron, or cobalt, which exert a decomposing action on the carbides, and which, becoming heated more easily than does the mixture which is to be converted into cyanide, yields to this mixture a part of its heat.

The examination of these methods shows that the inventor strove always to produce more and more, in a state as near as possible to the nascent state, substances which are to react upon one another. This is the object of the later patent dated December 31, 1900, and which allows the carbon monoxid produced in the reduction of the alkali oxids to be profitably utilized.

Lambilly proposes to collect this carbon monoxid in a gasometer, then to mix it with a quantity of illuminating-gas such that the hydrogen resulting from the decomposition of the latter may combine with the whole of the oxygen of the carbon monoxid, the acetylene thus formed yielding a fresh amount of carbon in the nascent state. This ingenious arrangement economizes more than half the illuminating-gas.

In his German patent No. 6377 (November 14, 1890, March 14, 1892), the only new fact given by Lambilly is the manner in which he obtains the alkaline mixture which is to be converted into cyanide. In order to make caustic the alkali or alkaline earth which is to be used in producing cyanide, carbonate of potash or of barium is used, and in order to render them porous and permeable to the action of the reacting gases, there is added for each equivalent of carbonate used (69 kg.  $K_2CO_3$  or 98 kg.  $BaCO_3$ ) 20 kg. of charcoal and a like amount of quicklime. The whole is worked up into a dry powder, introduced into horizontal cylinders connected with a vacuum pump, and heated under as perfect a vacuum as possible. Under these conditions the carbonate becomes caustic, and the carbonic acid produced by the reaction is reduced on contact with the charcoal into carbon monoxid, which is utilized as fuel. The inventor also states the amount of pressure under which he transmits the mixture of illuminating-gas and nitrogen into the cyaniding cylinders. This pressure should equal 10–15 centimeters of mercury.

The processes of Lambilly are still far from being perfect; yet they are extremely interesting to remember. At the time of their appearance they produced certain practical results which were by no means to be despised. Besides they show a considerable progress over the first synthetic processes used, a progress obtained through a profound study of the complex reactions which take place in the formation of cyanides, and which are the result of wise observations and of the patient efforts of their inventor. One could almost affirm that they paved the way for the really synthetic processes.

The following processes produce cyanides by the action of nitrogen on a mixture of caustic alkali or carbonate of alkali and charcoal. They differ but little from one another.

**Gilmour's Process.**—First comes this process (French patent No. 233175, October 2, 1893; German patent No. 8475, September 2, 1893). It consists in producing cyanide compounds by the action of atmospheric nitrogen on a mixture of alkali and charcoal heated to 1000°.

The various caustic alkalis or their carbonates may be used at will; however, the inventor prefers the use of caustic potash. These substances are mixed in about equal proportions with charcoal, the mixture is placed in suitable recipients through which nitrogen extracted from air is made to pass until the mass is more or less transformed into cyanide. The vessels are then emptied and the resulting product treated with water. The hydrocyanic acid of the cyanides in solution is displaced by means of a current of carbonic acid (this is preferably done at boiling temperature and under atmospheric pressure), and absorbed in a concentrated solution of caustic soda, where it forms sodium cyanide, which is separated. The carbonic acid is produced by the combustion of charcoal in air, an operation which allows the production of nitrogen necessary for the first reaction. Moreover, this carbonic acid produces anew the alkali used for the cyaniding process.

**Young's Process.**—This process (English patent No. 24856, Dec. 27, 1893) is but slightly different. The cyanide is obtained by passing a mixture of air and hydrocarbon vapors over the following mixture heated at a high temperature in iron or earthen retorts or in suitable furnaces:

Caustic or carbonate of alkali.. . . .	4 parts
Hydrate or carbonate of alkaline earth. . . . .	1 part
Coke or coal. . . . .	2 parts

The resulting product is treated with water in order to extract the cyanide. When the temperature is too high a portion of the cyanide distils. This portion may be collected by causing the gases with which it is carried away to pass through a layer of vegetable fibres.

**William Donnell Mackey's Process.**—This process (French patent No. 243136, Nov. 25, 1894; German patent No. 87366, Nov. 28, 1894) is quite similar to that of Bunsen. It consists simply in subjecting to a powerful current of air a mixture of coal, wood charcoal, or coke, lime, potash, or any other alkaline compound which may be reduced by the charcoal. This mixture is charged in a specially constructed furnace *A* (Fig. 3) through the hopper *E* and heated to a very high temperature. The furnace is vertical and quite large. It is provided with lateral openings to which are joined two series of tuyères. These are arranged in two series, *BB* and *CC*, one at one eighth the height of the furnace, the other at about the middle.

The cyanide formed is sucked away by a machine through the opening *D* situated in the space included between the two series of tuyères.

These are worked by a powerful bellows. The cyanide is collected and condensed according to ordinary methods.

The gases produced through combustion escape through the horizontal pipe *F*.

**Readmann's Process.**—Readmann's process (French patent No. 243129, Nov. 26, 1894, March 12, 1895) differs from Gilmour's process just cited only in the fact that the inventor uses the electric arc in order to produce the necessary temperature. In this way he claims that all waste and destruction of apparatus is avoided because he develops the heat in the very mass itself by means of carbon electrodes or electrodes of other suitable materials.

The mixture to be converted into cyanides is composed as follows:

Carbonate of barium (perfectly dry).. . . .	50 kg.
Powdered charcoal (wood charcoal or oil or coke). . .	10 "

The carbonate of barium may be replaced by any other carbonate or oxid of alkali or alkaline earth.

The intimate mixture of these substances is introduced into the crucible which contains coke previously heated to incandescence. As source of nitrogen the inventor uses air more or less deoxygenized, or water-gas, whose denitrified residue may be used either as fuel or for illuminating purposes. The cyanide formed flows out through

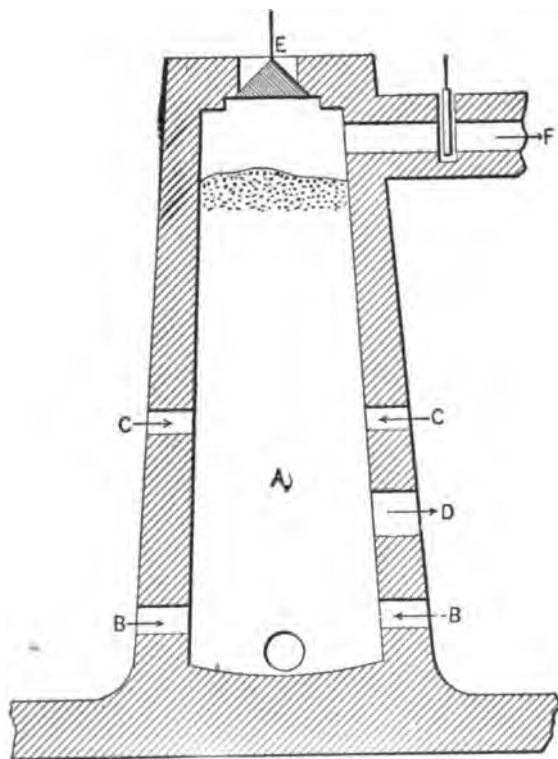


FIG. 3.—Mackey's Process.

a lateral opening situated on the bottom of the crucible. The volatilized portion carried off with the remaining gases passes into a receiver or condenser, where it is absorbed by well-known methods.

**Mehner's Process.**—Ch. Mehner of Charlottenburg has patented a similar process, which consists in passing a current of hot air, or

of any other gas rich in nitrogen, over a mixture of coke and carbonate of alkali or alkaline earth heated to a white heat in the vat of an electric oven. The volatilized cyanide together with the other gases are conducted into a system of condensers filled with coke placed above the level of the electrodes.

**Swan and Kendall's Process.**—In order likewise to avoid the wear and tear of the apparatus, Swan and Kendall have devised an ingenious though complicated arrangement the net cost of which must be quite high (French patent No. 252071, Nov. 24, 1895, and March 13, 1896, and German patent No. 87786, Nov. 28, 1895). It consists of an inner vessel constructed of thin sheets of nickel or cobalt, surrounded by another larger vessel made of refractory earth. This apparatus is placed in an oven which is slightly inclined. The inner vessel is provided with a platinum extension. Hydrogen circulates in the annular space between the nickel vessel and its refractory sheath; its object is to prevent the metal from being attacked. First a mixture of carbon and tungsten is prepared, consisting of 100 parts of the former to 15 parts of the latter, by moistening granular or powdered charcoal with a solution of potassium tungstate, drying, and igniting. This mixture is placed in the inner vessel; a current of nitrogen extracted from air is passed through and the temperature raised to redness. When this temperature has been attained, melted carbonate of potash in variable amounts is poured into the crucible. The cyanide formed flows out through the platinum extension as fast as it is produced. Tungsten may be replaced by titanium, molybdenum, chromium, or manganese.

**Pestchow's Process.**—In his process, Pestchow of Dantzic (German patent No. 94114, Dec. 8, 1896) has not introduced any great modifications.

It consists in causing a current of nitrogen containing or free from oxygen, mixed with or free from ammonia, and carrying a certain amount of hydrocarbon—e.g. acetylene—or powdered charcoal, to act on an alkali bath kept in a state of fusion. This bath is placed in a covered crucible provided with an opening through which the nitrogen gas mixed with hydrocarbons passes. The nitrogen should always be in excess, but not the carbon. To the alkali bath may be added a certain amount of cyanide from a pre-



vious operation in order to raise the temperature of the fused mass.

**Chipmann's Process.**—The latest process of this class is that of Chipmann, at Johannesburg (French patent Nos. 275570, March 4, 1898, and 275488, March 9, 1898), which produces at the same time cyanide and sulphocyanide by the action of a current of nitrogen to which sulphurous acid has been added, on a mixture of charcoal and oxid or carbonate of alkali or alkaline earth.

First a mixture of equal parts of charcoal and oxid or carbonate is made. Preferably, carbonate of barium is used.

This mixture is heated to about  $1000^{\circ}$  in suitable vessels; then a current of sulphurous acid free from oxygen is passed until the whole mass has been converted into cyanide and sulphocyanide. When this result has been attained, the vessel is emptied and the product treated with water. Into the solution thus obtained, heated to boiling and after the addition of an oxidizing agent, when necessary a current of air is made to bubble under atmospheric pressure.

The carbonic acid of the air precipitates the barium as carbonate, which is collected, dried, and used over again. The hydrocyanic acid set free passes into condensers containing a concentrated solution of caustic soda kept at a temperature of  $40^{\circ}$  F. The sulphurous acid produced by the decomposition of the sulphocyanide is collected with the nitrogen and used in the next operation.

Most of these processes have had but a short life industrially. That is because the circumstances which affect the yield are numerous, and a simple thing may change and at the same time modify the nature of the reactions. They are therefore but very imperfect methods, to which many and serious disadvantages are inherent.

The temperature necessary to carry on the reaction is in all cases very high: in some cases a white heat, in other cases a cherry-red heat. In all cases the heat must be sufficient to cause the reduction of the alkali compound used, and there are few apparatus which are capable of resisting such a high temperature without wear and deterioration. Another disadvantage of this high temperature is in the loss due to volatilization either of alkali or of cyanide, losses which sometimes amount to considerable. The substances used must also be as anhydrous as possible, water converting the

cyanide into ammonia. Nevertheless, Langlois, Kuhlmann, Armen-gaud, and Ertel have shown that the presence of a very small quantity of water helps along the reaction, for according to Kuhlmann the production of cyanogen is preceded by the formation of ammonia.

The mixture of substances to be converted into cyanide must be as perfect as possible, and all means must be taken to make it porous and permeable to the action of the reacting gases. The yield decreases in proportion as the cyanide is formed, for the fragments of the mass to be converted into cyanide, and especially the charcoal, becoming imbedded in the cyanide and melted alkali, come less in contact with the gases. If the contact surface of these substances is too small, the same trouble is met; the apparatus should be quite large in order to present as much surface as possible to the action of the nitrogenized gas. If care be not taken to remove the products as fast as they are formed, that also will impede the reaction, which will either be stopped or rendered slower.

If the substances under treatment contain foreign substances without effect on the reaction, these will absorb a portion of the heat, whence comes a loss of calories. Moreover, these bodies prevent the intimate contact of the products of the reaction.

Likewise, if the gases enclose foreign elements such as oxygen, hydrogen, carbon monoxid, or carbonic acid, they all have the disadvantage of diluting the nitrogen, which causes the reactions to go on more slowly. Moreover, each one of them exerts a detrimental action upon the reactions. Thus it is that carbonic acid oxidizes the charcoal, and possibly also the cyanogen. As has often been demonstrated, oxygen and cyanogen cannot coexist at high temperatures. As to carbon monoxid, some investigators attribute to it an injurious action in that it prevents intimate contact of the cyaniding masses with the nitrogen, whereas others look upon it as favorable to the reactions because of its reducing properties.

The formation of cyanides in these various processes has been the subject of much controversy.

Relying upon many experiments, and especially upon the fact that a mixture of acetylene and nitrogen, under the influence of the electric spark, yields hydrocyanic acid, Berthelot supposes

that when charcoal and potassa are strongly heated they give rise to a compound  $C_2K_2$ , which, fixing nitrogen, then yields potassium cyanide, CNK.

Most of the investigators agree in saying that the union of carbon and nitrogen can take place only at the temperature at which the alkali metal is set free. This hypothesis is confirmed by the very fact that cyanogen and oxygen cannot coexist in the same medium at a high temperature.

As to the alkali metal, some investigators attribute to it a simple contact action, and its object would therefore be to fix the cyanogen just as fast as it is formed, in accordance with the law of Sainte-Claire Deville, according to which reactions are continued and finished quickly if care be taken always to remove the products formed as fast as they appear.

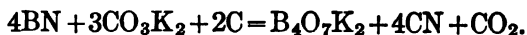
Finally, other investigators assert that there is first a formation of an alkali nitride, which later becomes converted into cyanide through the action of carbon. This last hypothesis is just as probable as the preceding ones, since Genter and Brieylieb obtained cyanide by heating magnesium nitride in a current of carbonic acid or carbon monoxid.

Several processes have even been proposed along this line, e.g. those of Moïse (French patent 246587, April 22, 1895) and of Mehner (French patent 254273, Feb. 26, 1896).

**Processes of Moïse and Mehner.**—Moïse's process consists in heating, in a rotatory oven to a dull red, a mixture of boron nitride, alkali carbonate, and charcoal in the following proportions:

Boron nitride.....	50 kg.
Carbonate of alkali (potassium). ....	250 "
Charcoal.....	30 "

The reaction is as follows:



Boron nitride is obtained by heating to a bright red for one hour the following finely powdered mixture:

Sodium borate.....	100 kg.
Sal ammoniac.....	150 "

This product is treated with boiling water, then hydrochloric acid is added in excess, yielding a precipitate of boron nitride.

Mehner prepares nitrides of boron, silicium, magnesium, titanium, and vanadium by reducing the oxids of these metals by means of carbon in the midst of an atmosphere of nitrogen.

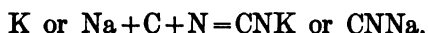
There is very little probability that these processes have given any practical results, and we doubt very much whether they have ever been operated industrially.

Besides, the metals which these investigators used in the preparation of the nitrides are too expensive to allow these processes to be used practically on an industrial scale.

All these processes just described have the disadvantage that they do not produce the cyanide directly; in fact, masses contaminated with impurities are obtained which must be treated with water and purified, by which the net cost is increased. It has already been seen that other equally serious disadvantages are inherent to these processes.

It has already been stated that the cyanide is formed only in case the alkali metal is set free. It was therefore quite natural that attempts should be made to use this metal in the free state in order to avoid the reduction of its compounds originally used and consequently the many disadvantages resulting therefrom. These processes may really be designated as synthetic, since they start with three bodies in the free state: carbon, nitrogen, potassium or sodium. The low cost of the alkali metals and the ease with which they are at present manufactured permit their use on an industrial scale. Moreover, the cyanide industry creates, by means of these processes, a new market for the sodium; its use became limited when it was no longer employed in the manufacture of aluminum. The experiments carried on along this line have been satisfactory. They are exceedingly interesting and they will therefore be described.

**Castner's Process.**—This, the first one of these processes, was patented by Hamilton Young Castner (No. 239643, June 28, 1894). It consists in the action of a current of nitrogen on charcoal heated to redness, upon which melted sodium or potassium flows, the reaction being as follows:



The reaction is carried on in a vertical iron retort (*A*, Fig. 4) placed in a furnace and capable of being heated to redness. This retort is provided with an inlet tube *B*, an S-shaped opening at the bottom *C*, and with a hopper *D*.

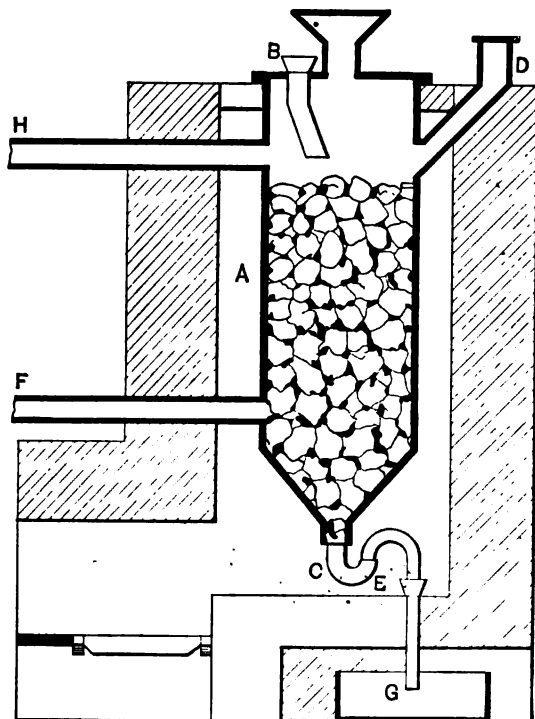


FIG. 4.—Castner's Apparatus.

The retort is charged with wood charcoal through the hopper *D*, which is afterward closed. The opening at the bottom *C* is sealed at the elbow *E* by means of cyanide. The temperature is raised to redness, then a current of nitrogen, through the tube *F*, and melted sodium or potassium, through the inlet tube *B*, are let in simultaneously. The alkali metal flows gradually through the wood charcoal and meets the nitrogen, which flows in the opposite direction. The three elements combine directly and form cyanide, which flows through the opening *C* into the receiver *G*. The unabsorbed gas escapes through the tube *H*, whence it may with advantage be conducted into a second retort. Charcoal may be replaced by

inert substances such as pieces of iron or of porcelain, in which case a mixture of nitrogen and hydrocarbon is conducted through the mass. The alkali metals may also be replaced by their alloys, e.g. lead sodium.

Castner has improved this process, which consists in using ammonia, and conducting the operation in two stages. This modified process will be taken up at length when discussing the ammonia processes. Castner's process, properly speaking, belongs to that class of methods using atmospheric nitrogen, the only one to which the term synthetic really belongs, but to our knowledge it has never given results permitting its use industrially.

**Hornig and Schneider's Process.**—This process belongs to the same class as that of Castner. Castner's process consists in allowing nitrogen to act upon the vapors of the alkali metals in the presence of incandescent charcoal; Hornig and Schneider's process uses the alloys of the alkali metals and of the heavy metals. Both of these processes using nitrogen or ammonia indifferently, but preferably the latter, will be studied in detail in the chapter devoted to the ammonia processes.

**Mehner's Process.**—Mehner's process (1894-1895) belongs in some respects to that class of processes using atmospheric nitrogen.

It consists in electrolyzing barium cyanide in a state of igneous fusion, using a charcoal cathode and in the presence of nitrogen gas (Fig. 5).

The current decomposes the barium cyanide into hydrocyanic acid, which escapes at the anode, and barium, which is set free at the cathode at a rather high temperature, close to its boiling-point. Meeting the nitrogen, which is in contact with red-hot charcoal at the cathode, this metal reproduces cyanide of barium, which flows in the bath and is thus subjected to electrolysis. In this way the process may be continued. With the same quantity of cyanide somewhat limited, it suffices to supply carbon and nitrogen and to maintain the temperature desired. The hydrocyanic acid gas formed may be conducted outside and absorbed by well-known means, or may be fixed in the electrolyzer itself by the addition of sea salt, which under the action of the current breaks up into chlorine and sodium. The hydrocyanic acid set free at the positive pole in a separate cell may, by means of a suitable contrivance,

react upon the alkali metal displaced and yield cyanide of sodium directly.

The last class of processes utilizing atmospheric nitrogen is based on the use of metallic carbides. It has already been stated that many investigators, especially Berthelot, explained the formation of cyanides through the intermediary of carbides. In *Comptes Rendus*, 1894, 503, Moissan reported that when nitrogen is passed over heated carbides of calcium, barium, or strontium no reaction or union takes place. Frank and Caro showed that

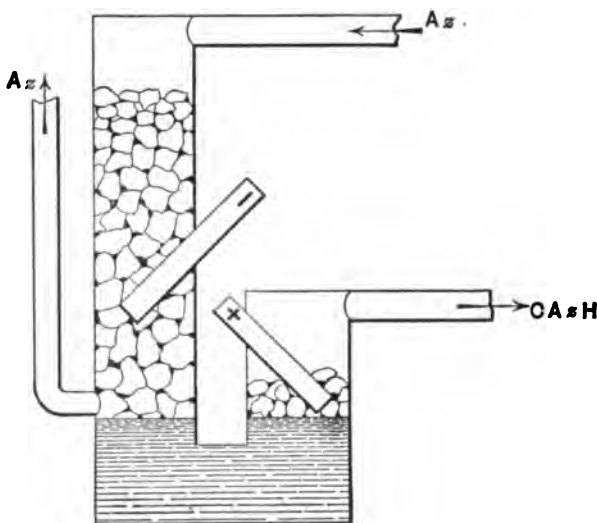
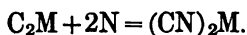


FIG. 5.—Mehner's Apparatus.

the opposite was true if the nitrogen used was charged with a certain amount of aqueous vapor. In this case cyanides are formed as follows:



Based upon this reaction, these investigators have brought out a process for the manufacture of cyanides which is thought to give satisfactory results. Many other manufacturers have followed the example set by Frank and Caro, and have had similar processes patented.

**Frank and Caro's Process.**—The first patent taken out by Frank and Caro dates from 1895 (French patent No. 249539, Aug. 10, 1895).

It consists practically as follows: It may be applied equally well to the carbides of the alkaline earths or alkalis, either pure or containing alkaline earths or alkalis, or even salts of these bases. A mixture of the carbides prepared in the usual manner may likewise be used; but according to the opinion of the investigators, barium carbide is the most suitable.

The carbide prepared in the usual way is disintegrated and introduced into a tubular retort of refractory material, preferably clay. This retort is provided with suitable tubes for the inlet and outlet of gases.

The necessary nitrogen is taken from the atmosphere. Air either wholly or partly free from oxygen may be used. The air is charged with moisture by passing it through a vessel containing water.

The retort is first heated almost to redness, then the current of nitrogen, charged with moisture, is admitted under a moderate pressure and at such a rate that the reaction is complete in about two hours. A change of 15 to 17 kg. barium carbide requires 2 to 2.5 cu. m. of nitrogen.

The product obtained is cooled, then taken up with water. The unconverted carbide yields acetylene, which is collected separately. The solution contains barium cyanide which by double decomposition may be transformed into alkali cyanide.

Carbide of calcium alone, thus treated, does not yield good results. An excellent yield is obtained, however, by using a mixture of calcium and barium carbides or of carbides of calcium and sodium obtained by the ordinary methods by means of soda lime and charcoal. The product of the reaction is treated as just stated—i.e. treated with water—the acetylene being collected separately and the solution thus obtained converted into alkali cyanide. This latter operation may be brought about either by addition of an acid or preferably by conducting carbonic acid through the solution, which displaces the hydrocyanic acid gas, which latter is brought in contact with the metallic oxid of the cyanide desired. This may likewise be effected by double decomposition by the addition to the solution of an alkali carbonate, which transforms the cyanide of the alkaline earth into alkali cyanide, while at the same time the carbonate of the alkaline earth separates out.



The result given by the treatment of the carbides of barium or calcium may be improved by adding to the carbides or to their mixture an alkali carbonate or hydrate.

When the alkali carbides, whether alone or mixed or even in the presence of an alkaline earth or its salts, are subjected to the same treatment as that indicated above in the case of the barium carbide, they yield the corresponding cyanides, which may easily be extracted with water from the product of the reaction.

The most favorable temperature for these reactions is, according to the investigators, dull redness. If a lower temperature be used the action of the nitrogen takes place but slowly, while if the temperature be too high the yield decreases, due to a partial decomposition.

In order to make the most profitable use possible of the nitrogen, several retorts may be used in a series, which allows a continuous operation.

In the certificate of improvement joined to the patent just described, Frank and Caro replace nitrogen with ammonia.

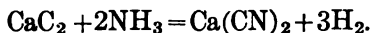
The investigators state that in practice the formation of cyanides depends not only on the action of free nitrogen, in the presence of water-vapor, on the carbides, but also on the action of dry nitrogen upon impure carbides containing oxids, carbonates, and sulphates.

Moreover, the chemically combined nitrogen (ammonia or the oxids of nitrogen) may likewise be used in the formation of cyanides by means of carbides if the nitrogen compounds used furnish, during their action on the carbides, the necessary nitrogen, a result which is brought about through dissociation or reduction by means of carbides. From these remarks the investigators think that the oxids, carbonates, sulphates, or other salts induce the reaction in the same manner as does water-vapor, the use of which may thus be suppressed. This action of foreign salts is shown even when the carbides contain only very small quantities of them.

Likewise, with the object in view of avoiding the use of water-vapor, the inventors of this process recommend the use of ammonia, which renders the action of moisture superfluous.

If ammonia be passed over a carbide or a mixture of carbides, or a mixture of carbides and alkali salts, cyanide is formed. During this formation, the ammonia becomes dissociated into its constitu-

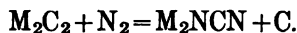
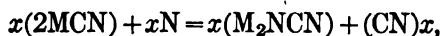
ent elements, nitrogen and hydrogen. The nitrogen becomes fixed to the metal, whereas the hydrogen escapes, and may be collected separately and used as such in the heating of the apparatus. The reaction may be thus interpreted:



Although the presence of moisture is useless in starting and completing this reaction, it does not modify it in any way, and exerts no perceptible action on the yield. Thus ammonia-gas, whether dry or moist, could be used equally with advantage.

Continuing their researches on the manufacture of cyanides by means of carbides, Frank and Caro observed:

(1) That the formation of cyanides by the processes above mentioned is however limited, and if the heating be carried on at least up to a dull redness and does not exceed a bright yellow, a large part of the nitrogen absorbed by the carbides is combined at the expense of the formation of other nitrogenous compounds. This phenomenon is, according to them, due in part to the action of cyanides already formed, and in part to the direct action of the reacting mass according to the two general equations



In fact Frank and Caro discovered that the reaction masses contained appreciable amounts of metallic derivatives of cyanamid,  $(\text{M}_2\text{NCN})$ , of paracyanogen  $(\text{CN})x$ , and of other nitrogenous compounds.

(2) That the formation of cyanamid in the action of nitrogen on carbides must be due to an excess of nitrogen, which condition may take place from the time that this gas comes in contact with the carbide.

(3) That the formation of cyanamid may be increased, by giving the carbide a greater surface, either by powdering it or by making it very porous and allowing the nitrogen to act, at a high temperature, varying from a dull red to incandescence, upon a thin layer of carbide. In this case it will be easily understood that the conditions will be eminently favorable for the formation of cyanamid,

a large quantity of nitrogen coming in contact with a small quantity of carbide. It is upon this series of remarkable observations that Frank and Caro have based their new patent, No. 289828, Oct. 2, 1899.

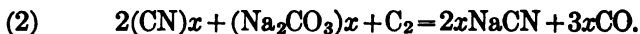
Carbide, or a mixture of two or more carbides, or of a carbide with other salts of alkalis or alkaline earth, is subjected to the action of nitrogen or of ammonia under the conditions stated above, with the view of favoring the production of cyanamid and of its derivatives.

The substance thus obtained is then converted into cyanide by fusing it with alkali hydrate or carbonate, which may be added to the materials of the reaction before or during fusion.

If the mass does not contain sufficient carbon, set free by the preceding reactions, it is well to add suitable quantities thereof.

Likewise, if the materials to be treated contain compounds of nitrogen which are not combined to a metal, e.g. paracyanogen, it is necessary to add a sufficient quantity of a base in order to combine the cyanogen formed.

This fusion results in converting the metallic compounds of cyanamid and of paracyanogen into cyanides corresponding to the bases used, according to the equations:



Generally the following are used:

Oxid or carbonate. . . . .	1 part
Salt of cyanamid. . . . .	2 parts

It is best to treat the product of the reaction with water, then to displace the hydrocyanic acid by an acid, e.g. carbonic acid.

The cyanamid remaining in solution is separated by shaking with ether or other solvent, or by other appropriate means.

While studying the ammonia processes a process will be noted which, although it does not utilize the carbides, has for its object the production of cyanamid. The solution of the problem seems to be along this line. Frank and Caro's processes certainly deserve to be kept in mind; they solve the problem quite satisfactorily and in an economic manner, seeing that the carbides are

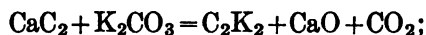
prepared with ease. We do not know whether these methods have been adopted on an industrial scale, though they were to have been tried in some Frankfort works. It was hoped that the experiments undertaken along this line would be crowned with success, since the use of carbides in the manufacture of cyanides would open, in fact, an important market for the former.

Unfortunately, it would seem that the works at Frankfort have stopped operation, the results obtained not having been thought sufficiently profitable for their continuance.

Other methods likewise based on the use of carbides have followed those of Frank and Caro.

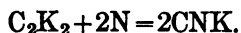
**Process of the "Chemische Fabrik Pfersée Augsburg."**—In the first place comes this process (French patent No. 252943, Jan. 3, 1896; English patent 1022, Jan. 15, 1896). It consists in allowing free nitrogen at a red heat to act upon a mixture of calcium carbide (or barium carbide) and dry alkali carbonate.

According to the investigators there would first be established a reciprocal reaction between the alkaline-earth carbide and the alkali carbonate, which in the case of calcium carbide and potassium carbonate may be thus expressed:

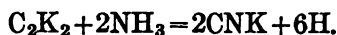


the carbonic acid would be immediately reduced to the state of carbon monoxid by means of a small amount of calcium carbide in excess.

The potassium carbide formed would then absorb the nitrogen according to the equation



The reaction takes place still better in the presence of ammonia:



The inventors propose to apply this property of the carbides to the old process of manufacture, which consists in using alkali carbonates, organic animal substances, or nitrogenized charcoal, and to ignite the whole at a high temperature. By adding a carbide to these substances the reaction would take place at a lower

temperature than that thought necessary up to the present time and the yield which was relatively small would be increased.

The advantages which would follow from the process of the *Chemische Fabrik Pfersée Augsburg* would be the following:

(1) An appreciable decrease in the cost of fuel, and wear and tear of the apparatus due to the relatively lower temperature of the reaction.

(2) The easy and abundant absorption of nitrogen.

(3) The obtaining, under the form of cyanides, of the almost theoretical quantity of ammoniacal nitrogen used.

These last two points should be verified industrially.

**Beringer's, Wolfram's, and Blackmore's Processes.**—Among the other methods using carbides must be mentioned that of Beringer (German patent 20334, Feb.–Nov., 1897), which consists in passing nitrogen over carbides, noting that the conversion into cyanides is complete at 900°, if dry and pure nitrogen be used, a condition which would complicate the solution of this problem from an industrial standpoint (the inventor claims that the reaction begins even at about 450° C.).

Wolfram's method (1898) consists in causing a metallic carbide (alkaline?) and a nitrogenous compound or free nitrogen, preferably ammonia, to act upon an alkali hydrate in state of fusion.

Blackmore's method (U. S. patent No. 605694, June, 1898) seems to complicate instead of simplifying matters. The inventor proposes to compress the nitrogen into a mixture of alkali sulphide and metallic carbide, preferably carbide of iron. The sulphide becomes converted into the corresponding cyanide, more or less contaminated with ferrocyanide and sulphocyanide, according to the amounts of the charge and the conditions of the reaction, conditions which are, moreover, not stated in the patent. Besides, the complete purification of this product must be rather expensive, and the author of the patent refrains from stating what is necessary in order to bring it about. This process, which is of little value, does not deserve deep study.

**Dziuk's Process.**—Very interesting, however, is the method of Dziuk (French patent No. 286828, March 15, 1899).

Dziuk of Hanover uses the alkaline-earth carbides, as do Frank and Caro, not, however, at the temperature of redness but at that of igneous fusion (1300–3000°), the nitrogen also being previously

heated at a high temperature. This modification is based on the fact that nitrogen acts on the alkaline-earth metals and on magnesium only at a very high temperature. This fact led the author to believe that nitrogen likewise should act on the carbides only at a temperature at which their constituent elements are in a free or nascent state. And, in fact, he was able to observe that if a current of nitrogen, heated to a high temperature before coming in contact with the carbide, be made to pass over calcium carbide manufactured in an electric furnace, this latter substance is converted into cyanide so long as it remains in the liquid state.

Here is how Dziuk in his patent explains this phenomenon. The nitrogen is first absorbed by the metal yielding a nitride which uniting with free carbon forms cyanide.

In practice, Dziuk uses any kind of electric furnaces which is used in the manufacture of carbides. Into the fusion chamber, at right angles to the electrodes, opposite the charcoal tube enclosing the fusion mixture, he introduces a second charcoal tube which serves to conduct the atmospheric nitrogen which has been carefully freed from carbonic acid, moisture, and oxygen, and which has been highly heated.

Thus, a brown-colored product is obtained which is composed almost entirely of cyanide and contains but a minimum amount of unconverted carbide. It appears best to allow the mass to cool somewhat in the nitrogenous atmosphere of the furnace.

Carbide in the process of formation in the electric furnace may be used or else carbide already formed, which however must first be subjected to fusion. This process is applicable to all the alkaline-earth carbides and to magnesium carbide, likewise to a mixture of these carbides.

These gases which issue from the furnace may be used in heating the nitrogen, and the cyanides obtained may be converted into alkali cyanides by double decomposition.

Dziuk comes to the same conclusion in an improvement to this patent by heating magnesium or lime in an electric furnace under the action of a current of nitrogen, then adding carbon in the form of coke in small portions. All this without interrupting the current. Under these conditions there is first formed a nitride which the carbon converts into cyanide.

**Process of the General Electrochemical Co.**—The last process to be mentioned, which makes use of carbides, is that of the General Electrochemical Company (French patent No. 299655, April 24, 1900). Like Dziuk's method, this process consists in causing nitrogen to pass over carbides in an electric furnace, but with this difference that the carbides are prepared in a special manner so as to make them more porous, and therefore more permeable and of greater surface for the action of nitrogen.

To attain this state of porosity, coke is added to the carbide which renders it more fusible, or else the carbide is prepared with an excess of carbon.

In practice, the following is the method of procedure: granulated carbide is mixed with coarsely ground coke and the mixture introduced into the incandescent electric furnace. The presence of this coarse coke brings the charge into a state of porosity which is very favorable to the absorption of nitrogen. The carbides of the bivalent elements are particularly suited to this purpose, for they are unsaturated compounds, each carbon atom having four chemical affinities, two of which may be united to a bivalent alkaline-earth metal, leaving three free affinities to each carbon atom. With these compounds it is quite easy to pass from the unsaturated to the saturated state by adding new elements having the smallest number of satisfied affinities. If nitrogen be passed through a heated mass of porous carbide, each molecule of carbide absorbs two atoms of nitrogen in order to become saturated, the three affinities of each carbide molecule being replaced by the three affinities of each of the two atoms of nitrogen, it being understood that carbon has a greater affinity for nitrogen than for itself.

The best way to obtain carbide porous enough for the manufacture of cyanides consists in mixing and pulverizing barium carbonate with an amount of coke greater than that necessary for the manufacture of barium carbide. The most convenient proportions to use are 3 parts of barium carbonate and 2 parts soft coal. This mixture is subjected to carbonization in an ordinary retort furnace. The result is a porous mass of coke in which the barium carbonate is found firmly fixed to the cellular walls.

This mass is transferred to an electric furnace which rotates continuously and subjected to a sufficient heat to produce barium

carbide. This substance fuses on to the particles of coke present in excess, forms a porous carbide, which afterwards easily absorbs the nitrogen at a temperature below that of the fusion of the carbide, yielding a cyanide of barium which may be separated by solution and crystallization.

Such are the synthetic processes which utilize atmospheric nitrogen. As may have been noticed, the progress achieved along this line has been remarkable. Of all these methods, five or six only deserve to be kept in mind, viz.: those of Lambilly, Margueritte, Sourdeval, Castner, and those of Frank and Caro, Dziuk, and of the General Electrochemical Company. It is very doubtful if the others can be profitably exploited.

#### B. PROCESSES UTILIZING AMMONIA.

Nitrogen being such an inert element, and its fixation being often laden with difficulties, it was sought to utilize ammonia whose chemical activities are much greater.

Liebig was one of the first to show that the ignition of nitrogenous organic substances in the presence of an alkali forms ammonia which in contact with charcoal heated to incandescence becomes converted into ammonium cyanide. Upon these data are based the processes of Karmrodt, Lucas, and Brunquell for the profitable conversion of animal substances into cyanides.

To Scheele, however, belongs the credit of having shown that ammonia may contribute to the formation of potassium cyanide. Scheele had even invented a process based on this observation and which consisted in heating a mixture of ammonium chloride, charcoal, and potassium carbonate.

Somewhat later Clouet demonstrated that when ammonia was passed over incandescent charcoal a soluble substance was obtained having a bitter-almond taste, and which in all probability was ammonium cyanide, according to the reaction

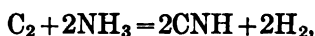


Langlois likewise obtained a similar result, and noticed the formation of small prismatic crystals of ammonium cyanide.

When a mixture of carbon monoxid and ammonia was passed over platinum sponge heated to redness, Kuhlmann likewise confirmed the formation of ammonium cyanide.



Weltzien also obtained a similar result. All these investigations are but laboratory experiments, and the investigators often found themselves opposed to one another; nevertheless to them belongs the credit of creating experiments on an industrial scale. Moreover, the question is still obscure enough. In 1897 Bueb and Bergmann demonstrated that when ammonia acts on incandescent charcoal there is formed not ammonium cyanide but hydrocyanic acid, according to the equation



while according to Lance (*Comptes Rendus*, April, 1897) the product of this reaction is always ammonium cyanide.

In the course of his experiments on the action of ammonia on charcoal at different temperatures, Bueb showed that at 800° the formation of hydrocyanic acid is quite small, i.e. about 4% of the nitrogen used; that at 1000° the yield increases to 24%, but from this temperature on the rest of the ammonia becomes dissociated.

He noted that the result was quite different when a mixture of ammonia and illuminating-gas was used instead of ammonia alone. In that case, even at 1150–1180°, three fifths of the nitrogen of the ammonia are converted into hydrocyanic acid, one fifth of the ammonia is obtained as hydrogen and nitrogen from the dissociation of the ammonia, and the remainder is not dissociated.

Repeating Bueb's experiments, Bergmann came to the following conclusions:

1. The action of ammonia on charcoal heated to redness gives, indeed, hydrocyanic acid, and not ammonium cyanide.

2. The addition of illuminating-gas to ammonia causes an increased yield of hydrocyanic acid and increases the resistance of ammonia to dissociation.

By working with a gaseous mixture containing 8–14% ammonia by volume, at a temperature between 1100 and 1180°, Bergmann observed that 19–52% of the nitrogen was used and converted into hydrocyanic acid, 69.2 to 19% was found in the state of ammonia, and 11 to 41% as free nitrogen. Moreover, the yield varies in inverse ratio to the velocity of the gases.

3. If, instead of illuminating-gas, hydrocarbons of higher molecular weights be used, the yield of hydrocyanic acid is not increased but

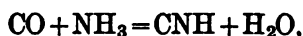
rather diminished, which fact seems to prove that nascent carbon has no action on ammonia.

4. If the illuminating-gas be replaced by carbon monoxid, the yield is about the same, but the amount of dissociated ammonia is greater.

Below are the results obtained by Bergmann.

Duration of Experiment.	Temperature.	Per Cent $\text{NH}_3$ by Volume.	Per Cent of N used in Form of $\text{CNH}$ .
hr. min.			
1 —	1130	46	28.1
1 —	1020	37	33.4
1 20	1100	17	39.9
1 —	1100	17	42.0
50	1130	17	39.5
33	1130	17	36.2
1 35	1130	10	44.2
45	1100	8	56.4
1 6	1100	5	43.7

5. The increase in the yield of hydrocyanic acid, confirmed in the experiments made with mixtures of ammonia and carbon monoxid or illuminating-gas, is not due to the chemical action exerted by this gas, as one would be led to believe, according to the equation



but it is the result only of the dilution of the ammonia-gas. In fact, in many experiments made with carbon monoxid and ammonia without the intermediary of wood charcoal, Bergmann proved that only 0.4 to 0.6% of the nitrogen used in the form of ammonia was converted into hydrocyanic acid, 32.5–62.2% was found as ammonia, and 34–68% in the form of free nitrogen.

6. The most favorable temperature for the formation of hydrocyanic acid depends materially on the nature of the gases used in diluting the ammonia. It is from 1000 to 1100° for carbon monoxid, generator gases, and mixtures of hydrogen and nitrogen; 1100° at least for the various gaseous hydrocarbons. At this temperature the dissociation of the ammonia decreases as the molecular weights of the hydrocarbon increases.

Compared with the results of Bergmann those of Lance present striking analogies, while at the same time differing considerably.

While studying the action of ammonia-gas on charcoal heated to redness, Lance observed (*Comptes Rendus*, April, 1897) that if dry ammonia-gas be passed over wood charcoal at the rate of four liters per hour, at a temperature between 1000 and 1100°, (1) ammonium cyanide is always formed; (2) the yield is greatest at this temperature; (3) the nitrogen combined under this form is equal to 25% of the nitrogen used under the form of ammonia.

If the ammonia-gas be diluted with hydrogen and nitrogen, the results are quite different.

1. If the ammonia constitutes  $\frac{1}{9}$  of the gaseous mixture, the yield in nitrogen converted into cyanogen is increased to 30.6%.

2. This yield increases with the increase of the quantity of hydrogen in relation to the nitrogen, and may reach 89.66% if the nitrogen constitutes but  $\frac{1}{10}$  of the volume of hydrogen.

3. Under these conditions at least 70% of the nitrogen of the ammonium cyanide comes from the free nitrogen of the mixture, i.e., from the nitrogen of the air.

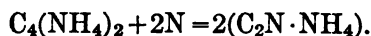
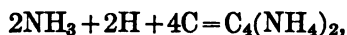
From these results, which are similar and yet contradictory, the conclusion reached is that the action of ammonia-gas alone, or mixed with other gases, on incandescent charcoal, is not at all well known. It requires still considerable study. Probably the action of the carbon is only one of contact, as is the case in many chemical reactions. This hypothesis is all the more probable if one recalls how Bergmann was able to obtain only traces of cyanogen by the action of nitrogen on carbon monoxide in the absence of charcoal, and, on the other hand, Kuhlmann obtained appreciable quantities of ammonium cyanide by working with the same gases, but in the presence of platinum sponge heated to redness. Be that as it may, these investigations have been the point of departure of several processes based on the action of ammonia upon incandescent wood charcoal.

**Lance and Bourgade's Process.**—First comes the method of Lance and Bourgade (French patent No. 265932, 1897). In this process ammonia is used only as the carrier of hydrogen and nitrogen. Under the name hydrogen the authors mean all the gaseous hydrocarbons,

gas, water, etc., and by nitrogen is meant either pure nitrogen or in the form of mixtures, such as air and the products of combustion of manufacturing establishments.

This process is based on the following reactions: If a mixture of acetylene and nitrogen be made to act upon one another in the presence of intense heat, there is formed hydrocyanic acid. The richer the mixture is in hydrogen, the nearer to the theoretical yield is the amount of hydrocyanic acid. It is at a maximum when the volume of hydrogen is at least two and one half times that of the hydrogen combined in acetylene.

If therefore a mixture of nitrogen, hydrogen, and ammonia be passed over carbon, there is formed an acetylene carbide of ammonium,  $C_4(NH_4)_2$ , which is only a transition product with which free nitrogen combines, yielding the compound  $C_2N \cdot NH_4$  or ammonium cyanide:



The yield approaches the theory in proportion as the conditions stated above relative to the mixture of the three gases, nitrogen, hydrogen, and ammonia, are adhered to. In their German patent No. 100775, taken Aug. 22, 1897, Lance and Bourgade give the following proportions:

Ammonia-gas.....	80 liters
Hydrocarbon.....	2000 "
Nitrogen of air.....	200 "

The ammonium cyanide obtained is then treated by well-known and appropriate methods to convert it into alkali cyanide.

**Mactear's Process.**—This is a somewhat similar process (U. S. patent No. 654466, July 24, 1900, French patent No. 292639). It consists in passing a mixture of carbon monoxid and ammonia-gas through a specially constructed chamber filled with wood charcoal or other suitable catalytic substance heated to 1800–2000° by means of electrical resistances.

The mixture of the two gases is previously made in a closed chamber in the proportion of two volumes of ammonia-gas and

one volume carbon monoxid. This gaseous mixture is then conducted through the decomposition chamber. The carbon monoxid should be pure; it is produced by passing a current of carbonic acid over coke heated to redness. The ammonia is obtained by the decomposition of ammonium sulphate with lime.

The gaseous products consist, for the most part, of ammonium cyanide. This latter product is then converted into alkali cyanide by treating it with a corresponding amount of alkali hydrate in a water or alcoholic solution.

The ammonia of the ammonium cyanide is set free and collected the solution of alkali cyanide is then evaporated.

**Process of the Stassfurter Chemische Fabrik.** — This process belongs to that class which utilizes the reaction of ammonia on charcoal. It is based on the following facts: When a current of ammonia is passed over a mixture of alkali or alkali carbonate and charcoal heated to dull redness, there is formed, indeed, a cyanide, but only in small amount, whereas a considerable amount of cyanate is produced.

The result is quite otherwise if the ammonia-gas be conducted through at a dull-red heat, and if after this adduction has ceased the heat is increased to full redness; the cyanate at first formed is reduced to alkali cyanide.

Gruneberg, Flemming, and Siepermann have patented a cyanide furnace (German patents Nos. 38012, 1886; 51562, 1889; French patent No. 200492, 1889) which has precisely the object of utilizing these reactions.

The manufacture of cyanide takes place in two stages in vertical retorts, several of which are placed in the furnace and comprising many parts; one part is heated to dull redness where the cyanate is formed, the other part heated to full redness where the cyanate is reduced to cyanide.

These retorts, *A* (Figs. 6 and 7), are enclosed in the furnace *B* with flues and placed in such a manner that the lower part of them is heated to an intense red, while the upper part is heated to a dull red. The lowest part of the retorts, *C*, is situated outside the furnace. It serves as a cooler for the cyanide formed, which is then collected in the receiver *D*, whence it is carried off by an endless canvas *E*. The mass, which is to be converted into cyanide, com-

posed of bits of wood charcoal impregnated with potassium carbonate, falls in virtue of its own weight from that part the least heated into that part which is heated to intense redness. It is introduced through the hoppers *FF*, which are afterward closed.

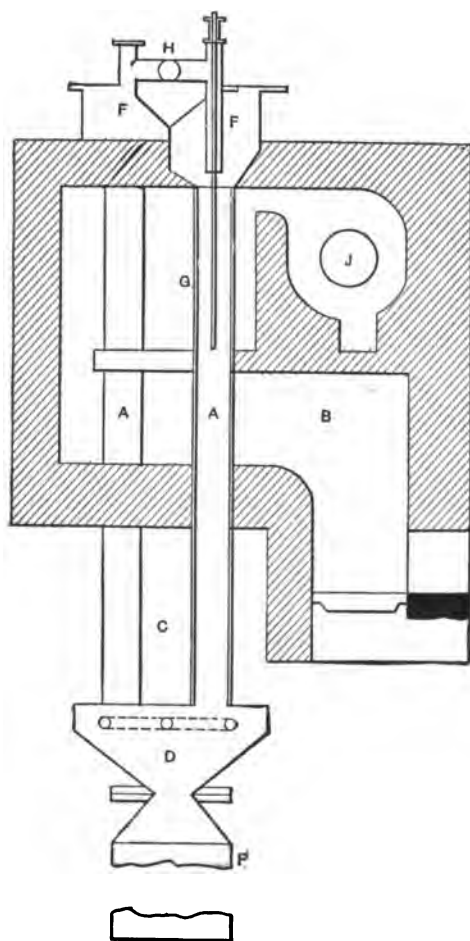


FIG. 6.—Apparatus of the Stassfurter Chemische Fabrik

As soon as the desired temperature has been reached, the tube *G* is pushed so as to bring about the lower opening at the point where the dull-red zone begins.

Then a carefully regulated current of ammonia is allowed to

pass through. The products of the reaction fall slowly into the receiver *D* and are carried off by the endless canvas *E*. The hopper *F* is filled at regular intervals. The gases, set free during the reaction, go out through the tube *H*, in whose axis is the tube *G* conducting the ammonia. A revolving drum, *J*, situated in the lateral flues of the furnace and heated by the flames escaping from the latter, permits the charge to be dried beforehand, for it should not be used in a moist state. The mass obtained is systematically treated with water until the solutions show a specific gravity of 40° B. The liquor is then treated with carbonate of potash either

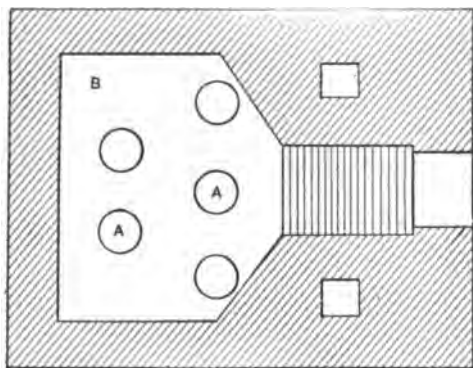


FIG. 7.—Apparatus of the Stassfurter Chemische Fabrik.

at ordinary or at a higher temperature. The greater portion of the potassium cyanide separates immediately if the work be carried on at ordinary temperatures, or crystallizes on cooling if carried on at a higher temperature.

The Stassfurter Chemische Fabrik, formerly Forster & Grunenberg, which has installed this process in its works, has at the present time 52 such furnaces, which are regularly operated, and which, it seems, give splendid results. It would appear that negotiations were in progress last year between a French company and the German company for the installation of this process in a chemical works near Paris.

**Moulis and Sâr's Process.**—This process (French patent No. 265715, March 26, 1897) likewise makes use of the action of ammonia on charcoal. The necessary ammonia is produced from the nitrogen of the air in the following way:

Air under pressure is blown into a vat-like furnace containing a certain quantity of small pieces of wood charcoal or cinders of coke. First there is formed carbonic acid, which passing through the red-hot charcoal of the upper zone is converted into carbon monoxid. This oxid of carbon, together with a small amount of carbonic acid and undecomposed air, passes before a reservoir of air so placed that this air becomes thoroughly mixed with the oxid of carbon so as to produce its complete combustion. In this way a mixture of nitrogen and carbonic acid is obtained together with a considerable amount of calories which may be used in heating the apparatus. The carbonic acid is absorbed by potash or sodium hydroxide and the nitrogen stored in a gasometer.

On the other hand, hydrogen is produced according to well-known methods (zinc and acid of  $20^{\circ}$  B.). When this hydrogen passes through nitrogen, at suitable temperatures, ammonia is formed. This latter gas passes through a refractory tube heated by means of oxid of carbon, and into which dehydrated and liquefied tar flows. Under these conditions the tar is vaporized, the vapors coming in contact with the ammonia and forming ammonium cyanide, which is collected in water and afterward converted into alkali cyanide.

The action of ammonia (substituted for nitrogen) on the oxids, carbonates, and metals of the alkalis, in the presence of charcoal, has likewise been tried. The processes of this kind are quite numerous and will now be passed in review.

**Lambilly's Process.**—Lambilly, whose remarkable researches have been discussed at the beginning of this chapter, is one of the first to have tried, with some success, to replace nitrogen, either partly or wholly, by ammonia. Having remarked that the reactions were conducted with greater ease if the carbon was in the nascent state, Lambilly thought that this advantage would be still more manifest if the nitrogen also was in this state, and with this end in view he proposed to substitute, partially or wholly, the nitrogen with ammonia. In his French patent (No. 223868, Aug. 26, 1892) he works as follows: He uses a mixture of hydrocarbon-gas and ammonia-gas with the optional addition of free nitrogen. This mixture is decomposed at a high temperature in the presence of an alkali or alkaline-earth compound and charcoal.



The cyaniding mixture is obtained in the following way: A concentrated solution of carbonate of potash or caustic potash or caustic soda is made, into which is poured pulverized charcoal at the rate of 100 parts per each 100 parts alkali. This mixture is evaporated to dryness, then to it are added 20–30 parts powdered lime and 50 parts iron filings, and the whole is massed together into the form of briquettes with the aid of tar or other like substance. These are then ignited in iron retorts or cylinders heated to bright redness in such a way as to reduce as much as possible the alkali compound and to convert it into a state favorable for the absorption of nitrogen. This operation is best carried on in a vacuum. When this is finished, this point being indicated by the cessation of the liberation of gas ( $\text{H}_2\text{O}$  or  $\text{CO}_2$ ) according to the alkali compound (hydrate or carbonate) used, the gaseous mixture of ammonia and hydrocarbon with or without free nitrogen is made to pass through. The latter gas is produced by passing air over copper heated to redness, and the oxid of copper formed serves in carburating the hydrocarbon-gas. This hydrocarbon-gas should preferably be quite dense. It may be profitably obtained by heating charcoal impregnated with heavy coal-tar oil in cylinders at a temperature between 50 and 300°.

The gaseous mixture passes over the cyaniding substances under a slight pressure, in order to bring it into intimate contact with all the particles of this substance. On issuing from the retorts the gases are recarbureted. The mass so obtained is withdrawn from the cylinder and treated with water. In the claims of his patent Lambilly states the following advantages of his process:

1. A great rapidity.
2. It permits, in a single operation in a definite amount of alkali, the amassing of more cyanide than any other process at the time known.
3. It is therefore very economical.

**Beilby's Process.**—This process, dating from the same year (French patent No. 219156, Feb. 4, 1892), does not present any great improvement over the processes then known, and besides the net cost must be quite high. It consists in passing a current of ammonia through a melted mixture of anhydrous caustic alkali, cyanides, and finely powdered charcoal heated at a high temperature in a

suitable apparatus. The addition of cyanide is to lower the point of fusion of the mass, in order to avoid deterioration of the iron receptacles in which the operation is conducted.

The amounts stated by Beilby are:

Pulverized charcoal. ....	20 to 25%
Potassium carbonate. ....	55 " 60%
Potassium cyanide. ....	20%

The apparatus used are retorts or pots of iron provided with a tube for the inlet of ammonia, an outlet tube, a hopper, and a tap-hole.

The ammonia may bubble through the melted mixture, or else the mixture may be subjected to an energetic stirring by means of a mechanical stirrer during the passage of the current of ammonia.

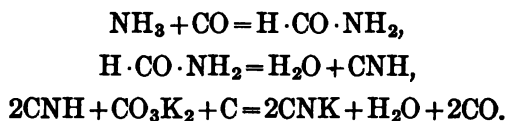
It is important always to have some potassium cyanide in the mixture during the operation, and in such amount that the mass remains fluid, without, however, producing foam, which might obstruct the exit.

The cyanide which in part is volatilized is collected in a system of condensers. The operation may be so conducted that the whole of the cyanide is volatilized. Ammonia may be substituted by the alkaloid bases of the pyridine series.

As was remarked, this method must be rather expensive because of the amount,  $\frac{1}{5}$ , of cyanide added to the other products.

The substitution of the alkaloid bases for the ammonia is not profitable. Besides being expensive bodies, they are quite resistant to high temperatures and an appreciable amount of these bodies thus escape decomposition.

**Young and Macfarlane's Process.**—The method of Barr, Macfarlane, Mills, and Young (English patent No. 3092, 1892; French patent No. 230066, May 13, 1893) is somewhat different. It is based on the action of a mixture of ammonia and carbon monoxide on a fused mixture of alkali hydrate or carbonate and charcoal, according to the general reactions:



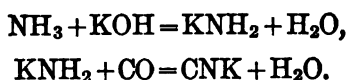
The most suitable proportions are:

Caustic potash .....	100.0 parts
Charcoal (wood charcoal or coke).....	22.5 "

This mixture is heated at 815° C. in a retort or other receptacle, then a current of carbon monoxid and ammonia is passed through, either separately or previously mixed, and heated if thought necessary. Under these conditions there is formed a cyanide corresponding to the base used, which may afterward be separated and purified according to ordinary methods. The gases which come out of the retorts may be used over again after being enriched with the one or other necessary constituent.

As a profitable source of ammonia and carbon monoxid, the authors recommend using the gases of blast-furnaces or other industrial furnace gases, likewise gases from slate-retorts or from gas-works, after purification, if they are thought suitable.

Under these conditions the authors claim a yield of 70%. Repeating the experiments of Young and Macfarlane under the most favorable conditions, Conroy was able to obtain a yield of but 30%. He remarked, besides, that the cyanide is formed very slowly, Macfarlane himself has, moreover, stated that 36 hours are required to produce a yield of potassium cyanide of from 60–70%. The longer the experiment continues, the more rapid becomes the formation of cyanide. This method, moreover, requires an elevated temperature, which causes a rapid wear and tear of the apparatus. Thus, in Young and Macfarlane's experiments, the steel tube which was used in carrying on the reaction was reduced, at the end of 36 hours, to the thickness of an ordinary sheet of paper. Conroy repeated the experiment with a cast-iron tube and noted a similar wear. According to him the reaction would take place as follows:



According to the authors of the patent there would be formed formamide, which would then break up into water and hydrocyanic acid, which latter would be absorbed by an alkali.

Conroy's hypothesis presupposes the formation not of formamide, but of potassamide. According to his idea, the formation of cyanide is due rather to a simultaneous action of the three substances present, and probably with the formation of potassamide as an intermediary product. Moreover, Beilsten and Geuther had previously established the fact that the oxid of carbon reacts on the potassamide with formation of potassium cyanide. Repeating this experiment by heating potassamide in a glass tube at 50–600° under the action of a current of carbon monoxid, Conroy was able to obtain a yield of 35% potassium cyanide. He considered, however, that if instead of a glass tube he had used an iron tube, the yield would have been almost theoretical. Without deciding in favor of either one or the other of these two suppositions, both equally established, it will be seen further on that the latter seems more probable, judging from the results recently obtained with a new process the object of which is the intermediary production of alkali amides. Nevertheless, since these data have not yet been confirmed experimentally we will rely on the results obtained.

**Chaster's Process.**—This process (1894) does not present anything very new or characteristic. It simply consists in passing ammonia which has been previously dried over quicklime, over an intimate mixture of coal and a carbonate of an alkali or alkaline earth. As in Lambilly's process, this mixture is prepared by adding powdered coal to a concentrated solution of carbonate, evaporating to dryness, and igniting.

**Pleger's Process.**—This process (German patent, No. 89594, Aug. 7, 1895) also does not differ much from the preceding ones. It consists likewise in causing a current of ammonia to act on a mixture of alkali and charcoal heated to 900°. The author, however, does not add at once the whole of the charcoal necessary. Only a portion of it is used, the rest being carried in gradually with the ammonia-gas which is blown into the crucible. Ammonia charged with pulverized charcoal is continually blown in until there is no longer any liberation of hydrogen or of carbon monoxid. When this point has been reached the mass is allowed to remain in quiet

fusion, and the melted cyanide is filtered in order to separate it from the excess of charcoal. As in all the preceding processes of this class, the ammonia may be replaced by nitrogen, either of the air or in the form of the mixture which the local combustion of carbon in excess produces.

These various processes, which are more or less similar, produce greater or less amounts of cyanide, the yield, however, never being equal to the theoretical, and Conroy estimates, and not without reason, that  $\frac{2}{3}$  are lost. One of the causes of this failure is to be found in the resistance which the cyaniding mixture presents to the action of ammonia-gas. Now, one of the essential conditions of success is that the mixture allow the gaseous current to circulate freely while being intimately penetrated by it.

**Roca's Process.**—Roca in his French patent No. 266550, May 3, 1897, seems to have realized this desideratum. For this purpose he first brings his cyaniding mixture to a special physical condition of porosity, which is especially suited to assure the most perfect and most economical absorption and circulation of the ammonia throughout the mixture and its transformation proceeds into cyanide.

Roca starts with the idea that this mixture should not be so fine as dust, but rather in small pieces which will leave spaces between each other large enough to allow the circulation of the gas and permeable enough to this gas that the action will not be confined to the surface. Moreover their weight should not be such as to cause the pieces to become crushed, and therefore they should maintain a certain degree of hardness.

Toward this end he mixes finely ground wood charcoal, ground in the presence of water so as to lay the excessive dust, with the purest commercial potassium carbonate in the proportion of 30-35 parts of charcoal to 65-75 parts carbonate. He adds 10-20% water so as to make the mass homogeneous and slightly moist. Thus prepared, this mixture when squeezed in the hand should form a soft ball.

This mass is then spread out and pressed into thin layers upon a metallic floor capable of being heated. The potassium carbonate dissolves in the small amount of water contained in the mixture and then it imbibes the charcoal, the whole forming an intimate mass.

The mass then becomes turgid and coherent, and under the influence of heat the small quantities of air and water-vapor seek to escape, leaving small cavities in the interior of the mass. Finally, after drying completely, there is obtained a sufficiently hard charcoal, which resists being crushed, which is very homogeneous, porous, and at the same time of very low specific gravity (density 0.45–0.55), and which may be cut up into briquettes. This mass is kept out of contact of air and moisture until it is to be used.

This mass is charged into vertical cast-iron retorts which are hermetically covered and provided at the lower part with a vane, forming an air-tight joint during the cyaniding process. It is only necessary to open this vane to make the cyanided product flow into a sheet-iron extinguisher.

These retorts are arranged in series of five or six in suitable furnaces. Each retort is provided with two tubulatures. One, placed near the cover, serves to admit the gases; the other, placed a little above the vane, serves as their exit. The bottom of the retorts are covered with pieces of dry wood charcoal so arranged as to avoid any incomplete transformation on account of lack of heat and to facilitate the exit of gases.

Uniform circulation and continuity of working are made sure by a system of pipes and suitable valves (see Fig. 8).

The arrangement shown in Fig. 8 permits one to understand the principle of the apparatus and the workings of the various taps. According to the cut, ammonia-gas is admitted into the apparatus by way of tap  $V_3$  in the retort  $C_3$ , which is the one earliest charged; it passes into retort  $C_2$  by means of  $X_2$ , and into retort  $C_1$  through  $X_1$ . From this retort the gas goes through the tap  $X_5$  into  $C_5$ , and through  $X_4$  into  $C_4$ ; then it flows into the exit tube through the tap  $Y_4$ . Every time a retort is cyanided, the order of using the cocks is changed and thus a continuous operation is permitted. By means of this arrangement any one of the retorts may be disconnected during the unloading and reloading without stopping the operation in the other retorts.

In this way a mixture of nearly pure cyanide and charcoal is obtained which, after cooling, may be treated with water and purified in the usual way. The residual charcoal, when well washed, may be used anew.

The gases which are discharged from the furnace are cooled and are then conducted into a tower filled with coke, where a thin stream of water circulates and holds back the entrained ammonia. Thence they are conducted under the hearth and used as fuel, for they liberate more heat than is absorbed by the endothermic reaction obtained in the retorts. In this way the expense of fuel is considerably lessened, and in fact it is, on this account, very small.

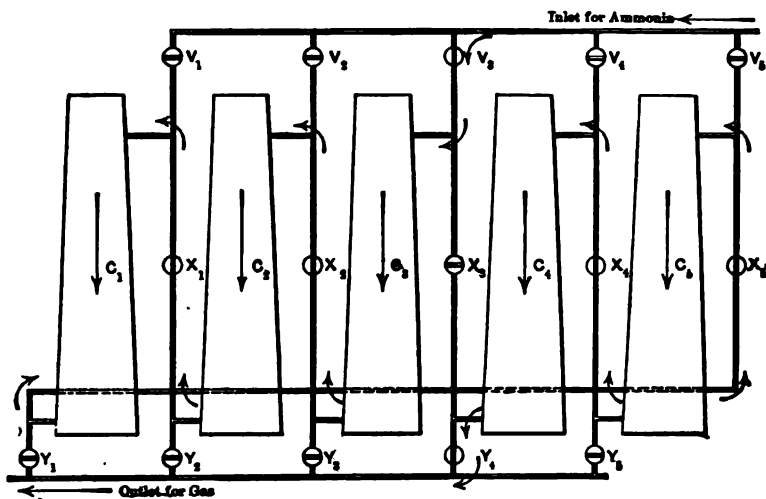


FIG. 8.—Roca's Apparatus (plan).

In an addition to his patent, Roca advises the substitution of barium carbonate instead of potassium carbonate, and this for several reasons.

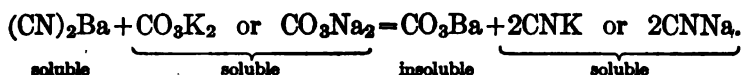
The cyanide obtained is very soluble and chemically pure, the barium carbonate being insoluble and not passing into the cyanide solution when the cyanide is treated with water.

Barium carbonate is not so expensive and it may be regenerated when the barium cyanide is converted into alkali cyanide. Moreover, at the temperature at which the reaction takes place (800–900°), carbonate of barium dissociates much less than does carbonate of potassium, and almost no soluble baryte is formed to contaminate the cyanide.

The cyaniding mixture is formed by mixing 100 parts of the

purest commercial carbonate of barium with 30–35 parts wood charcoal. Then are added 20–25 parts of a dilute and warm solution of gelatine in order to make the mixture cohere. After drying, the mixture is broken up into pieces of the desired size, and these are transferred to the apparatus described above and treated in the same manner.

The product thus obtained is treated with water, and after filtration the barium cyanide is converted into an alkali cyanide by the addition of an alkali carbonate according to the following reaction:



The precipitated barium carbonate is separated by filtration, and after drying, it may be used anew.

As may be seen, Roca's process is really ingenious, and it shows a marked improvement over all the preceding processes. Yet it is very doubtful if by this process, even, a theoretical yield can be obtained, a condition which is extremely difficult of fulfilment when the oxids or carbonates of the alkalis are used.

**Hood and Salamon's Process.**—Before taking up the study of processes working directly on the alkali metals themselves, which to our mind simplifies the solution of the problem very much, we cannot omit mentioning the very original and peculiar process of Hood and Salamon (German patent No. 15142, 1895–1896).

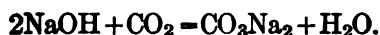
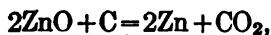
This process differs from the preceding in that it is worked not in the dry way but in the wet way. In an early patent (English patent No. 87613, Sept. 4, 1894) Hood and Salamon worked in the dry way. The alkali carbonate was treated with a reducing metal—zinc, lead, etc.—and this mixture was heated to redness in a current of dry ammonia. The reaction is as follows:



but only half of the alkali metal is converted into cyanide. In order to complete the reaction profitably the authors proposed that a current of heated carbonic acid and ammonia be passed



over the mixture, or that a bit of charcoal be added to the mass in order to reduce the cyanate formed as well as the oxid of zinc.



In the German patent (No. 15142, 1895-1896) Hood and Salamon operate in the wet way. If metallic zinc be in suspension in strong alkaline solutions to which carbonates or bicarbonates have been added, and a current of ammonia be passed through these boiling lyes with constant agitation, there is produced under these conditions alkali cyanide according to the same reaction as above.

As in the case in the dry way, only one half of the alkali is converted into cyanide. The reaction may, however, be completed by the addition of finely divided charcoal, which reduces the zinc oxid and carbonates to an equivalent quantity of alkali. The cyanide solution is then evaporated to dryness in suitable apparatus.

We do not know what results have been produced by this really peculiar process. One may truly ask oneself if the reactions do in reality take place as the authors state, and if the charcoal can really reduce zinc oxid under the conditions mentioned. These are points which require elucidation in order that this original method may be judged.

The disadvantages inherent to the use of the oxids or carbonates of the alkalis or alkaline earths for their conversion into cyanides, and to which we called attention when the processes utilizing free atmospheric nitrogen were studied, reappear in the ammonia processes using these same oxids or carbonates. The most serious of all, as we have seen, is the necessity of producing the high temperature required in the reduction of the compound used.

As in the processes using nitrogen, it was sought to remedy this by making use of the alkali metals themselves.

**Hornig's Process.**—The first process of this kind is that of Hornig. (German patent No. 15467, April 5, 1894; Feb. 21, 1895). This

process deserves to be mentioned especially on account of its originality. It consists in making the vapors (?) of the alkalis or alkaline-earth metals (?) (which are produced in a separate generator) act upon carbon in the presence of nitrogen or ammonia, or upon compounds of nitrogen and carbon.

The process is united directly with the electrolytic production of the alkali metals. When the vapors of these metals escape from the furnace they are conducted, by means of a current of water-vapor (?), into an inclosure which is highly heated and where they come in contact with proper amounts of carbon and nitrogen necessary for their conversion into cyanide. The carbon is supplied in the form of carbonic acid, carbon monoxid, hydrocarbon, or even finely divided wood charcoal; the nitrogen is supplied in the form of ammonia or of atmospheric nitrogen.

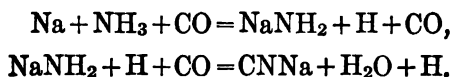
The cyanide formed immediately flows into a receiver—for example, a retort communicating with the lower portion of the apparatus, where it escapes all further reaction.

It is not indispensable that the alkali metal be produced electrolytically; it may be produced by any other apparatus and process known.

When nitrogen is used, the reaction may be written



and when ammonia and carbon monoxid are used the reaction is



The technics of this process must be most difficult, especially in that which relates to the production of the alkali metal vapors, and it is difficult to explain satisfactorily how these vapors are drawn off with the aid of steam. We doubt therefore if this process has been worked, or even set up for work, on an industrial scale. Nevertheless, since we knew of its originality we could not omit mentioning it, for it shows all the more how far the researches for the synthetic production of cyanides has been carried.

**Schneider's Process.**—This process (German patent No. 9775, June, 1894; Sept., 1895) has already been much improved. It makes

use of alloys of alkali metals and the heavy metals, such as lead, zinc, or tin, but preferably lead, and these are brought into reaction at high temperatures with nitrogenous and carbonized materials.

The advantages in using this method are: A better yield due to the greater specific weight of these alloys, their lesser tendency to oxidation, and their greater ease of handling than in the case of the free alkali metals. The author recommends using an intimate mixture of the alloy and nitrogenous and carbonized gases, stirring with a stirrer, or, better still, by injecting the gases into the melted alloy.

If the gas be brought in contact with the surface of the fusion only, the surface of the alloy soon becomes coated with a layer of cyanide, which makes any further conversion into cyanide impossible.

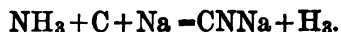
Here is how the author would proceed, for example, to produce sodium cyanide:

In an iron crucible 80 cm. high and 35 cm. in diameter, an alloy of lead sodium containing 10% of this metal is melted beneath a layer of sodium cyanide. Into this bath, heated to dull redness, is pumped a mixture of acetylene and ammonia in excess. The cyanide of sodium formed collects on the surface of the alloy, which grows less and less, finally leaving lead almost free from sodium.

A mixture of monomethylamine and ammonia may be used.

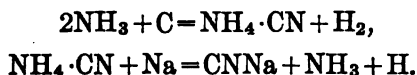
**Castner's Process.**—The process which, belonging to this type, seems the simplest and at the same time the most economical, and which appears to give the best results, is that of Hamilton Young Castner.

The process patented by Castner, No. 239644, June 28, 1894, is but a repetition of patent No. 239643 of the same date, which has already been studied in a previous chapter, but with this difference, that the author substitutes ammonia for nitrogen. The reaction may therefore be expressed:



The apparatus is the same as that used in the case of nitrogen. As the author states, one may also cause dry ammonia-gas to pass over heated charcoal, and the resulting gas, consisting of ammonium cyanide,  $\text{CN} \cdot \text{NH}_4$ , then passes over fused sodium, where it

becomes converted into sodium cyanide, with ammonia set free, which latter may be recovered and used again in the conversion of a fresh quantity of charcoal into ammonium cyanide. In this way the reaction is continued with a small amount of ammonia. The reactions are:

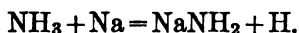


Castner has been led to confirm that practically in both these methods, either the nitrogen or the ammonia process, intermediary reactions are produced, due more or less to the temperature and to the proportion of constituents present, which reactions make the manufacture rather difficult unless numerous inconvenient precautions be taken to avoid loss of metal or of nitrogen.

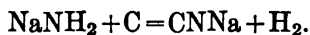
These observations led him to modify his process, which he did in the French patent No. 242938, Nov. 17, 1894.

In this new process the operation takes place in two successive stages, so that the yield obtained is almost theoretical, according to the author, and the general character of the method is simplified. Moreover, this important modification allows the process to be carried on in a continuous way.

In the first stage of his process, Castner seeks to produce an alkali amide by passing anhydrous ammonia-gas over sodium heated at a temperature of 300–400°, according to the reaction



In the second stage he converts this amide into cyanide by bringing it in a melted state in contact with charcoal:



In practice the process is carried on by means of two retorts. In the first retort, specially constructed, the description of which will follow, the conversion of the alkali metal into amide takes place, and in the second, which is somewhat similar to that used by Castner in his first process, the second phase of the process takes place, i.e., the conversion of the amide into cyanide.

One half of the rectangular retort *B* (Figs. 9, 10, 11) is provided with partitions *C*, which reach low enough to plunge into fused

metal *D*. The ends of these partitions are cut short in order to allow the gas or vapors to follow the direction indicated by the

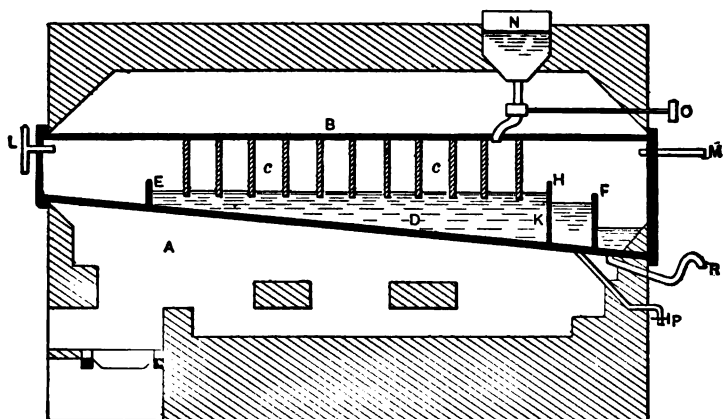


FIG. 9.—Castner's Process. Furnace (A) with Rectangular Retort (B) (Elevation).

arrows. The upper half of the retort is provided with a forked entrance tube *L*, an exit tube *M*, a bent tube with hopper *N* pro-

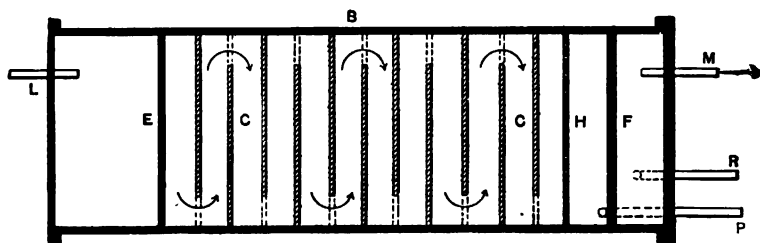


FIG. 10.—Castner's Process. Perspective of Half of the Retort.

vided with a valve *O*. The lower half is lined with partitions *E* and *F*, the former reaching a little above the level of the latter, and with the partition *H* reaching a little below partition *F*. It contains several openings shown in *K*.

The bottom of the retort is provided with an exit tube *P*, and another one *R*. The rectangular retort is composed of iron.

The following is the method of procedure in practice: The retort *B* is heated to 390–400°, then dry ammonia-gas is conducted into it, through the tubes *L* and *L'*, in order solely to expel the air. When this is done, the sodium, which is melted in *N*, is allowed

to flow up to the level of the dotted line between *E* and *H*. The flow of the metal is then for the time being stopped.

The intake of ammonia is regulated according to the capacity of the retort; the sodium flows only at regular intervals, that is, for every 17 kg. of ammonia, 23 kg. of sodium are required.

The amide which forms at the surface of the bath melts and sinks to the lower part. It fills the space included between *H* and *F*, driving the sodium out through the tube *R*. The overflow of amide thus becomes regulated and may be collected in closed vessels, being afterward subjected to the further treatment in the process

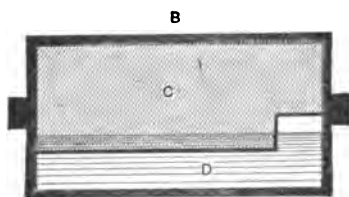


FIG. 11.—Cross-section of the Retort.

of forming cyanide, or else it may be transferred directly by appropriate appliances to the retort shown in Fig. 12, where the second phase of the process takes place. This second retort is filled with wood charcoal and heated to dull redness; the amide flows through the tube *S*, and the hydrogen formed escapes through the tube *W*, while the cyanide produced flows in *X*. From time to time fresh charcoal is added in order to replace that which has been used.

Castner is one of the few manufacturers who faced the problem of the synthetic production of cyanide at a favorable moment. His discoveries certainly mark one of the most important advances in the history of this interesting industry. His process has been taken up in Germany. Important improvements have been added, and the day is perhaps not far distant when a real synthetic process for the production of cyanide along this line will appear.

**Process of the Deutsche Gold und Silber Scheide Anstalt.**—Thus it is that the above important German firm has just recently taken out two patents, one for the preparation of cyanamide, the other for the preparation of alkali cyanides, both of which are based on the formation of alkali amides, and according to information we have been able to gather have given, up to the present time,

satisfactory results. These two patents present a lively interest, and the reader will take it kindly of us if we reproduce them here almost entirely.

The first of these patents (No. 308170) concerns the preparation of cyanamide. Up to this time this body had been considered difficult of preparation. Frank and Caro, in a process of cyanide manufacture which we have previously described, had already made

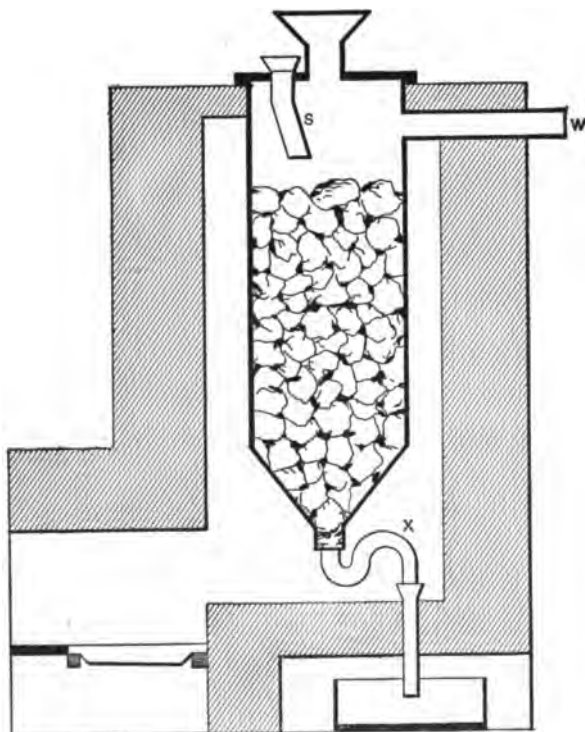


FIG. 12.—Castner's Process. Second Phase of the Process.

known a more practical means of preparing it on an industrial scale. The Deutsche Gold und Silber Scheide Anstalt has since that time been led to find a process, simple as well as practical, which allows its preparation in a really economical way.

The formula of cyanamide is  $\text{H}_2\text{N}\cdot\text{CN}$ . With metals it yields metallic compounds which may correspond to the formula  $\text{M}$  or  $\text{M}_2\cdot\text{CN}\cdot\text{N}$ . Thus, with sodium it yields monosodium cyanamide,  $\text{Na}\cdot\text{N}\cdot\text{CN}$ , and disodium cyanamide,  $\text{Na}_2\cdot\text{N}\cdot\text{CN}$ .

The dialkali cyanamide is prepared by the Deutsche Gold und Silber Scheide Anstalt, by starting with the alkali amide obtained, as is well known, by the action of ammonia on an alkali metal at a temperature higher than the melting-point, but lower than the point of the dissociation of the amide and the ammonia-gas.

The process is based on this still unknown fact that carbon at about  $400^{\circ}$  displaces hydrogen of the amide and yields cyanamide, while at a higher temperature, about  $800^{\circ}$ , it yields, as is known, cyanides.

If therefore carbon either in the solid state or in the form of hydrocarbon gas be brought in contact, at a temperature of about  $400^{\circ}$ , with an alkali amide prepared according to well-known methods, and in the melted state, cyanamide will be formed. Solid or melted amide may also be brought in contact with a solid bath composed of a body rich in carbon and heated to a suitable temperature, or likewise ammonia at a temperature of  $400^{\circ}$  may be conducted into a mixture of melted alkali metal and charcoal; but in either case, the temperature must be successively increased with the corresponding formation of cyanamide until this temperature be somewhat higher than the point of fusion of the cyanamide.

Such is the process for the preparation of the dialkali cyanamide as brought out by the Deutsche Gold und Silber Scheide Anstalt. It has resulted in obtaining in a practical way the synthseis of cyanides, as we shall presently see. In fact, when treated with charcoal at a high temperature the cyanamide becomes converted into cyanide. This method of the preparation of cyanides is an improvement over that of Castner, described above, in that the alkali amide used by Castner decomposes at a low temperature—above  $400^{\circ}$ —while cyanamide withstands a temperature up to  $800^{\circ}$ .

In practice the Deutsche Gold und Silber process is carried out as follows:

In a crucible mounted and built in a furnace which may be well and easily regulated, sodium is melted with charcoal or carbonaceous compound (hydrocarbon or other compound) in such quantity as will suffice to convert all of the metal into cyanide. When the metal has been melted, ammonia is then conducted at a temperature somewhat raised ( $400$ – $600^{\circ}$ ). Under these conditions alkali amide is formed which, under the action of a portion of the charcoal, becomes,



in its turn, converted into cyanamide dialkaline,  $\text{Na}_2\cdot\text{N}\cdot\text{CN}$ . By raising the temperature to  $700\text{--}800^\circ$  this cyanamide in contact with the remainder of the charcoal forms the final product, sodium cyanide,  $\text{NaCN}$ .

But as the cyanide (a body containing carbon) may also be used in the formation of cyanamide, the process may be so arranged that a portion of the alkali cyanide found in the crucible at the end of the operation may be always left therein in sufficient quantity to produce the cyanamide of the next operation, and only sufficient charcoal to convert this cyanamide into cyanide need be added. In any case a quantity of alkali cyanide corresponding to the alkali metal and the ammonia used is always obtained.

As may easily be seen, this process, which is very ingenious, is both practical and economical. Over all the methods thus far invented, it has the following advantages, which are to be attentively considered:

1. The operation is carried on at quite low temperatures, which prevents, to a considerable extent, loss either of alkali or of cyanide, as well as any deterioration of the apparatus.
2. The process requires only a restricted as well as simple apparatus, since the whole operation may be carried out in one and the same crucible.
3. The yield is quite high, and, according to the authors, is very near the theoretical.

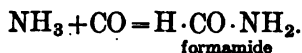
These advantages are certainly to be considered, and there is no doubt but that the process of the Deutsche Gold und Silber Scheide Anstalt will be applied on a really important scale, thus allowing the cyanide to be delivered at a remunerative price.

We have already called attention to the fact that many investigators had explained the formation of cyanides, resulting from the action of ammonia and carbon monoxid, through the intermediary of formamide. We have also seen that the accepted theory is rather that of the formation of potassamide. Yet several processes are based on the former hypothesis.

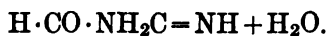
**Lambilly's Process.**—Lambilly, whose name appears at the head of most of the innovations of the cyanide industry, is one of the first to have based a process for the manufacture of cyanide on this class of reaction.

In his French patent (No. 232697, 1893) Lambilly carried on his new method as follows:

Into one or several tubes heated to a temperature between 40° and 150° and filled with porous substances, a mixture of carbon monoxid and ammonia is conducted, according to the reaction



This formamide, when heated at a temperature above 210° in a second group of tubes filled, as in first case, with porous substances, is decomposed with formation of hydrocyanic acid:



**Martin's Process.**—This process (French patent No. 262949, Jan. 11, 1897) consists in bringing atmospheric nitrogen into reaction with methane in definite quantities (the amounts are not indicated by the author) contained in a retort constructed of refractory brick which is charged with porous substances which have previously been metallized with platinum, titanium, vanadium, or magnesium. Under these conditions the methane breaks up into acetylene and hydrogen.

Under the influence of heat, nitrogen, and hydrogen, the acetylene in the nascent state is decomposed into gaseous cyanogen products, which are conducted into a cylinder adjoining the retort and containing fragments of potassa-lime heated to redness. In this way potassium cyanide is obtained, which may be separated by filtration and crystallization. We are not in possession of any further data concerning this process, nor of its working.

**Glock's Process.**—This process (German patent No. 108152, March 15, 1899) still utilizes the property which formamide has of breaking up into water and hydrocyanic acid.

Glock heats, in an autoclave at 200–300°, ammonium formate alone, or mixed with ammoniacal zinc chloride, yielding formamide which distils



its vapors being conducted over melted potassa or soda, or a mixture of the two, heated to 250–350°. If the formamide still contains

moisture and unconverted ammonium formate, the alkali should be heated above  $360^{\circ}$ . The reaction consists in dehydrating the formamide under the influence of the melted alkali, a dehydration which gives rise to hydrocyanic acid which becomes fixed immediately by the alkali with formation of cyanide.

Two other processes which are quite peculiar and original and which are based on quite different principles from those already studied will be mentioned.

**Huntington's Process.**—The first is that of Kirby Huntington (English patent No. 14855, Aug. 6, 1895; German patent, No. 16931, Jan. 1896, April, 1897; French patent No. 253740, Feb. 5, 1896).

In this method the inventor produces hydrocyanic acid by means of rapid deflagration of a mixture of equal volumes, or of 105 vols. nitric oxid and 100 vols. acetylene in a cylinder with firm walls:



The mixture of the two gases serves as a motive force for an ordinary gas-motor by the use of the electric spark.

The gases which issue from the cylinder pass through a series of absorption apparatus filled with strong alkali solutions. The hydrocyanic acid is absorbed and forms cyanides, whereas the hydrogen and the carbon monoxid are collected in a gasometer and may be used as fuel.

This process does not appear to us to have given satisfactory enough results to warrant its use industrially.

**Hoyermann's Process.**—The second of these processes is that of Hoyermann (French patent No. 294979, Dec. 5, 1899). It is but a modification of Huntington's process, in which it is sought to avoid the formation of carbon monoxid and hydrogen which takes place in that process. Instead of using nitric oxid, Hoyermann employs nitrogen, according to the reaction already indicated by Berthelot,



The reaction takes place in a carbide electric furnace. The electrodes are hollow and are used for the introduction of the acetylene and the nitrogen which they bring separately into the zone of action of the luminous arc. The mixture and the union of the two

gases take place at that point. Calcium carbide may likewise be produced in the furnace, and on the addition of water-vapor, acetylene may be formed. At the same time, the introduction of air, which comes into contact with the acetylene, yields hydrocyanic acid under the action of the electric arc. The hydrocyanic acid thus formed is removed by means of a suction-pump, collected and absorbed by suitable means.

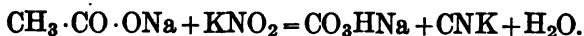
Moreover, the process may be made continuous. In fact, under the action of water-vapor, calcium carbide becomes decomposed into acetylene and lime, which latter, on careful addition of pieces of charcoal, may be intermittently transformed anew into carbide.

This process does not seem to us to be any better suited to industrial purposes than the preceding one.

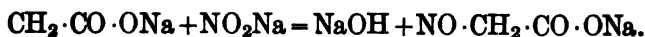
Nitric and nitrous nitrogen have also been employed.

**Roussin's Process.**—Roussin has noted that if a mixture of fused potassium acetate, potassium nitrate, and potassium carbonate be dissolved in a small amount of water and evaporated to dryness and the residue be fused, it deflagrates violently at 350°, leaving behind a black spongy mass containing a large quantity of cyanide of potassium mixed with potassium carbonate and charcoal. But this method has one disadvantage in that  $\frac{3}{4}$  of the carbon of the acetate is converted into carbonic acid by the oxygen of the nitrate. To overcome this disadvantage Roussin proposes the use of potassium nitrite mixed with lampblack, acetate, and carbonate of potash.

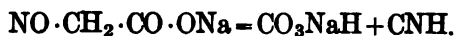
**Kerp's Process.**—Wilhelm Kerp (Ber. d. d. Chem. Gesell. 1897, p. 610) observed that when sodium acetate is fused with potassium nitrite, there is formed potassium cyanide according to the reaction



The yield of cyanide depends to a large extent on the temperature; in no case does it exceed 25%, and the reaction often yields considerable quantities of hydrocyanic acid. According to the inventor, the reaction should take place thus: In the first phase of the reaction there is formed caustic soda and nitroacetate of sodium:



This salt is then broken up into bicarbonate of soda and hydrocyanic acid:



A portion of the hydrocyanic acid thus formed combines with the caustic soda, the rest escaping. This is therefore a process which is not applicable to industrial purposes.

**Kellner's Process.**—This process (French patent No. 252282, Dec. 9, 1895) consists in subjecting to the electric arc an alkali nitrite or nitrate with or without addition of charcoal to facilitate the reaction.

Siepermann had previously tried to utilize the same reaction, but in a reverberatory furnace. With this object in view, he injected pulverized alkali nitrite or nitrate into a reverberatory furnace by means of compressed air, the furnace being charged with charcoal alone or charcoal to which had been added a small amount of carbonate. The cyanide formed flowed through a draft-hole situated in the most sloping place of the sole. As a portion of the cyanide formed became volatilized at the high temperature at which it was necessary to carry on the reaction, the gases escaping the furnace passed through condensation chambers or absorption towers, where they gave up this salt.

**Grossmann's Process.**—Jacob Grossmann's process (1900) is a rather curious one. It is based on the reaction, already known, that if liver of sulphur be melted in the presence of charcoal, and then ammonium sulphate be added to the fused mass, a very lively reaction (sometimes even an explosion) takes place which yields sulphocyanide of potassium. This process, studied by Fleck in 1863, had not been tried on an industrial scale. Grossmann took up the process anew, and modifying the nature of the reactions, made out of it a method for the direct manufacture of cyanides. He noted that if ammonia be passed over a mixture of liver of sulphur and charcoal heated to redness (700–800°), potassium cyanide is formed; sulphocyanide is formed only in a secondary way, the greater portion of the sulphur being converted into either hydrogen sulphide or ammonium sulphide.

If the sulphide already formed be used, the process requires

equal parts of sulphide and of wood charcoal; when liver of sulphur is used the following proportions are necessary:

Carbonate of potash (pure).....	100 parts
Charcoal. ....	120-140 “
Sulphur. ....	24 “

These quantities are necessary to prevent heaping together.

### III. SPECIAL PROCESSES.

Under this heading will be mentioned processes which have been proposed for the production of cyanides, and which do not belong to any of the preceding classes. According to information obtained by us, it follows that, with the exception of Dr. Bueb's process, the other processes have either not been tried at all or to a very limited degree; yet we shall mention them in order to show the variety of ideas brought out concerning the manufacture of cyanides, all of which indicate the interest and importance of this question.

**Process of the Chemische Fabrik Aktiengesellschaft.**—One of the most interesting processes of this class is that of the Chemische Fabrik Aktiengesellschaft of Hamburg (German patent No. 5242, 1894-1895, and French patent No. 241146, 1894-1895).

It consists in heating to redness sodium or potassium carbazol with or without the addition of sodium or potassium hydrate or carbonate, and in case it is desired to produce ferrocyanides, with the addition of iron.

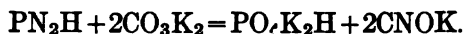
Carbazol is obtained in the residues from the purification of crude anthracene (by means of benzene, sulphurous acid, etc.), which residues contain large amounts of it. These residues are treated with dry or slightly moist caustic alkali corresponding to the amount of carbazol present. This treatment takes place in a cast-iron pot provided with a stirrer. Heat is applied gradually till the temperature reaches 260-280° when potassa is used, and to 320-340° with soda. This temperature is maintained for several hours. The alkali carbazol formed separates out clearly from the other compounds (hydrocarbons, etc.). It is collected separately and to it is added an excess of caustic soda or potash or their carbonates, and in, if the object be to prepare ferrocyanides. The mixture is then heated to bright redness. The fused mass is taken

up with water and treated according to any of the ordinary methods for the separation of cyanide or ferrocyanide.

In practice the method of procedure is as follows: 200 kilos of residue from the purification of anthracene, containing 40% or thereabouts of carbazol, are treated with 30 kilos caustic potash. The heat is kept at 260–280° until all the water separated by the union of the carbazol with the potassa has distilled, which requires about three hours. The stirrer is then stopped, and after a quarter of an hour's repose, the product is run into moulds. The whole solidifies; but after cooling, it is easy to separate the solid cake of potassium carbazol which lies at the bottom of the moulds from the more or less soft crystalline magma formed with floating anthracene carbides. The crude potassium carbazol is crushed and again heated in an apparatus similar to the one mentioned above, capable of being heated to bright redness. The temperature is gradually raised to this point, and under these conditions the potassium carbazol becomes converted into cyanide with separation of carbon and liberation of some ammonia and combustible gases. A greater yield may be obtained by carrying on the fusion in the presence of an alkali used as a flux. Unfortunately we have no data concerning the yield produced by this process.

**Vidal's Process.**—This process (German patent No. 2868, 1897; French patent No. 274875, Feb. 9, 1895) uses phospham.

If a mixture of 6 kilos of phospham and 19 kilos potassium carbonate be heated to redness up to complete desiccation of the phosphorus, there will be formed potassium cyanate and phosphate according to the reaction

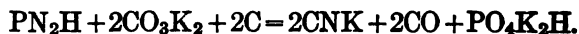


The mass may be treated with water or alcohol, which dissolves the cyanate, leaving the less soluble phosphate behind.

But if to the charge used above charcoal be added in the following amounts,

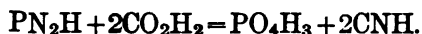
Phospham.. . . . .	6 kilos
Potassium carbonate.. . . . .	19 "
Charcoal.. . . . .	1½ "

cyanide of potassium will be obtained:



By adding 0.8 kilo of iron or 4 kilos of sulphur to the above charge ferrocyanide or sulphocyanide will be obtained.

The carbonate may be replaced by neutral or acid oxalate which yields cyanogen or hydrocyanic acid, which escapes, or the phospham may be heated to 150–200° with fatty acids. Thus, with formic acid, there is formed hydrocyanic acid:



The operation is carried on as follows: 60 kilos phospham are placed in an enamelled cast-iron pot and heated in an oil-bath to 150–200°. Then 48 kilos formic acid or 63 kilos acetic acid are rapidly run in. Hydrocyanic acid is collected by the usual means.

We do not know whether this process has been tried.

To conclude this last part, we shall take up certain processes whose object is to extract in the form of cyanide the nitrogen contained in the residues of the refinery and of the distillery. The molasses and vinasse contain, as is well known, variable amounts of nitrogen (0.5–2.5%). Various methods have been proposed for regaining this nitrogen in the form of ammoniacal liquors or of ammonium sulphate, but most of these methods have not continued in use for any length of time. The product obtained is largely contaminated with amines formed during ignition, which are difficult to separate from the ammonia. Among them are trimethylamine, dimethylamine, monomethylamine, monobutylamine, and monopropylamine. Moreover, the gases which escape during the distillation of the molasses and vinasses spread abroad in the surrounding atmosphere an odor which is tainted and injurious to the public health. Besides avoiding this disagreeable odor, Bueb's processes furnish cyanide cheaply and in a relatively simple manner.

**Bueb's Processes.**—In his first French patent (No. 246282, April 1, 1895) Dr. Julius Bueb conducts the gases which escape during the distillation of the vinasses and molasses into a system of vessels or refractory tubes heated to bright redness or to a white heat.



In this way all the volatile compounds of nitrogen which they contain are entirely converted into ammonium cyanide mixed with a little ammonium carbonate. On emerging from the system of tubes, the gases pass into suitable solutions (ferric salts).

The vinasses at  $40^{\circ}$  B. are introduced into the furnace *A* (Figs. 13, 14, 15, 16). Toward this end they are made to flow from the upper reservoir *a* into the receptacle *b*, and by means of a siphon *c* into the retort, where a liberation of gas immediately begins. The gases of the distillation are collected in the tube *e* and transmitted

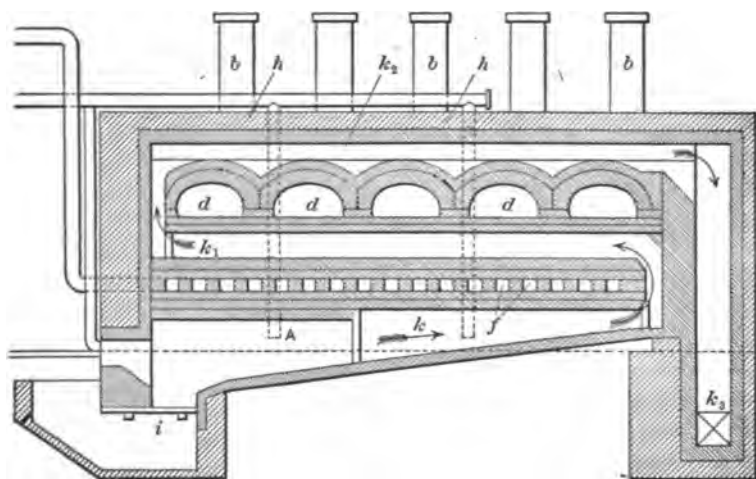


FIG. 13.—Bueb's Process.

directly into the pipes *f*. These pipes go through the furnace in zigzags, and are so arranged that the gases require about 15 seconds in passing through.

After passing through these pipes, the gases are conducted to the absorption apparatus. The heating of the furnace may be done by means of the gases from the distillation after first freezing them from the cyanogen compounds. They first heat the pipes *f* by passing under them by way of the passage *k*; then above, through the space *k1*; and lastly they likewise heat the retort by way of the passage *k2*. The temperature of the pipes is between  $1000$  and  $1100^{\circ}$ , that of the retorts  $700$ – $800^{\circ}$ .

By means of this process, Bueb obtains a gaseous mixture composed to a large extent of hydrocyanic and carbonic acids. In order to separate these two gases, he uses the same method that

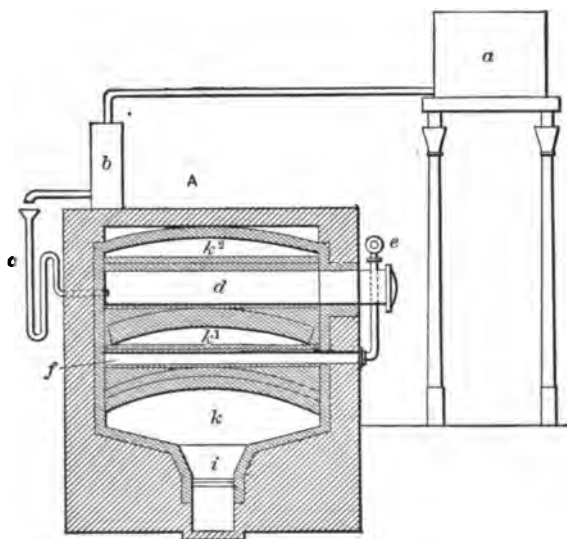


FIG. 14.—Bueb's Apparatus.

is used in extracting cyanogen from coal-gas; that is, its absorption by means of iron salts, the result of which being the formation of

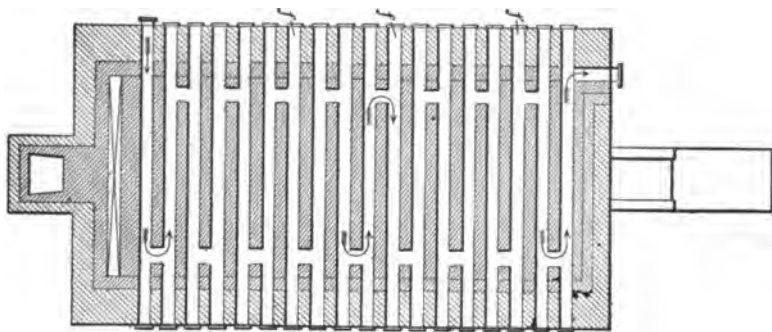


FIG. 15.—Bueb's Apparatus.

a double ferrocyanide which may then be converted at will into alkali cyanide.

Later, Bueb was led to separate hydrocyanic acid from car-

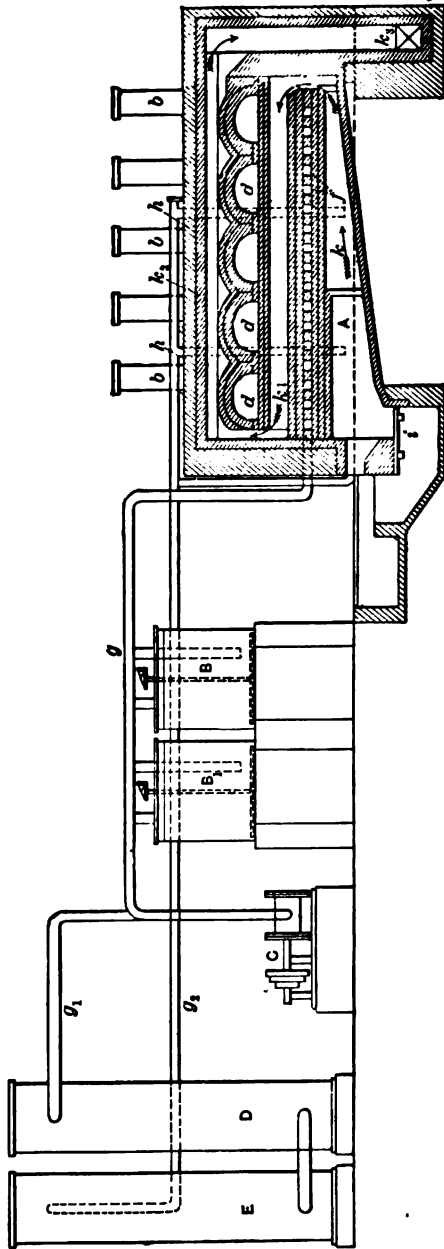


FIG. 16.—Bueb's Apparatus.

bonic acid directly in the form of alkali cyanide. To this end he proceeds as follows (French patent No. 283968, Dec. 13, 1898).

The gaseous mixture is first cooled down, and in case it contains ammonia, it is made to pass into dilute sulphuric acid (20%).

Thence it is conducted to a tower through which a stream of very strong alcohol flows in the opposite direction. The alcohol dissolves only the hydrocyanic acid, so that a solution of hydrocyanic acid flows at the bottom of the tower. This solution is subjected to a fractional distillation, and the vapors of hydrocyanic acid are then combined in the usual way.

For this purpose it is possible, and it is moreover the method which the author particularly recommends, to have the vapors of alcohol and hydrocyanic acid pass through an alcoholic caustic alkali solution. Alkali cyanide, which is formed, being quite difficultly soluble in alcohol, is precipitated in the form of a white powder. The alcohol is condensed and used again in repeating the operation.

After absorption, the vessels containing the lye, when cooled, are connected with an aspirator. After the aspiration, there remains in the apparatus practically pure alkali cyanide (98%). The mother liquors which flow from the aspirator, and which contain 2 to 4% alkali cyanide, are conducted into a saturation apparatus placed in front of the tower through which alcohol flows, and the gases passing through precipitate the alkali as carbonate, while the alcohol becomes saturated with the hydrocyanic acid which is converted into cyanide as before.

In his patent No. 296793, taken out in 1900, Bueb states that during the dry distillation of vinasses the gases which pass through the narrow tubes where the conversion into cyanide takes place deposit, when heated, particles of carbon which obstruct these pipes and hinder, to a considerable extent, the regulation of heat. In order to remedy this inconvenience, he proposes the following arrangement:

The distillation takes place in retorts filled with pieces of refractory substances previously heated to the required temperature. When this temperature has been reached, the heating is discontinued, and the gases are passed through. These gases become rapidly heated through the heat of these refractory contact-bodies and are converted into cyanide compounds. During this opera-

tion, the gases deposit upon these contact-bodies charcoal to such an extent that they become coated therewith. When this point has been reached, the supply of gases to this oven is stopped, and instead they are conducted to another oven already heated during this first stage of the process. During the second stage the apparatus, which has been exhausted, is heated anew, and at the same time the calorific power of the deposited carbon is utilized in heating the refractory contact-bodies for the next operation. Thus, the process may be carried on continuously, and besides, the deposited charcoal, which used to be a serious danger in the cyaniding process, is utilized.

Bueb's processes are used on an industrial scale to a considerable extent in Germany, where quite favorable results are obtained they are regularly in operation in one of the largest sugar-works. The raw salts of vinasses obtained appear to be better. In any case, the process may be easily adapted to refineries and distilleries without modifying in the least their usual course, and it would allow considerable extra revenue to be derived from the beet residues.

The idea is, moreover, not entirely new, for from 1894 the Société anonyme de Croix (Nord) manufactured cyanides from trimethylamine. As is known, this compound, corresponding to the formula  $N(CH_3)_3$ , is obtained in large quantities in the dry distillation of beet residues. It is formed by the decomposition of the two alkaloids found in beet-juice, betaine and cholin. The ordinary molasses may contain as much as 5-13% betaine. From Bressler's investigations, it follows that in 100 parts of nitrogen of beet residues, 20.67 parts belong to betaine and 20.32 to cholin; and in 100 parts nitrogen in the products of distillation of the beet residues, 26.76 parts are in the form of trimethylamine. Moreover, most of the alkaloids, on decomposing, yield trimethylamine, and the distillation of wood also gives a certain amount of it.

**Ortlieb and Muller's Process.**—The process of the Société anonyme de Croix is due to Ortlieb and Muller, and is based on an old reaction pointed out by Wurtz (*Ann. de Chim. et Phys.* XXX, p. 454), which is as follows: If trimethylamine be passed through a porcelain tube heated to redness, there is formed hydrocyanic acid and ammonium cyanide.

Ortlieb and Muller's process is simply the application of the

above reaction. Commercial trimethylamine is first vaporized in specially constructed boilers. These vapors are then conducted into retorts similar to those used in gas manufacture, and heated to redness, when they are broken up into hydrocyanic acid and ammonium cyanide. The products of this decomposition are conducted through a series of absorption apparatus. The first series contains dilute sulphuric acid. The ammonium cyanide is there decomposed into sulphate of ammonia, which remains in solution, and hydrocyanic acid, which together with that already formed in the gaseous mixture, passes on into the other absorbers. These contain either sodium or potassium hydrate, or milk of lime, or any other alkaline-earth hydrate.

The alkaline solutions absorb the hydrocyanic acid, yielding concentrated solutions of the corresponding cyanides, while the residual combustible gases, completely freed from prussic acid and ammonia, are collected in a gasometer and used as a source of illumination. This process allows the recovery, in the form of ammonium sulphate and cyanide, of the whole of the nitrogen of trimethylamine.

## CHAPTER VII.

### MANUFACTURE OF FERROCYANIDES.

**FERROCYANIDE** of potash, or yellow prussiate of potash, has long been, together with Prussian blue, the only cyanide compound known and manufactured. It served a long time as the basis for the manufacture of cyanides, and at the present time 50% of the ferrocyanide produced is still used for that purpose by means of the processes which were reviewed at the beginning of Part I.

Ferrocyanide may be produced in an industrial way by two distinct classes of processes:

- (1) Those based on the use of nitrogenous organic substances.
- (2) Those which utilize the spent oxides from the purification of illuminating-gas, or those whose object is to extract the cyanide compounds directly from this gas.

Other processes have been likewise proposed. But most of them produce cyanides as intermediary compounds, and they have been studied in the previous chapter. It should also be mentioned that all the synthetic processes proposed for the production of cyanides may likewise be employed in the manufacture of ferrocyanides, either by adding metallic iron to the cyaniding substances or by treating the cyanided masses with strong solutions of ferrous salts.

The present chapter will consist of two parts:

- (1) Manufacture of ferrocyanides by means of nitrogenous substances.
- (2) Manufacture of ferrocyanides by means of illuminating-gas or of the masses which have served in its purification.

## I. OLD PROCESSES BASED ON THE USE OF NITROGENOUS ORGANIC SUBSTANCES.

These processes were for a long time the only ones employed in the manufacture of potassium ferrocyanide. At the present time they have almost wholly been abandoned, there being but a few works (in Germany, England, and the United States) still in operation. However, as many important studies and investigations have been conducted along the line of these processes, and, moreover, as the industry of the cyanide compounds is derived from them, we shall describe them more or less at length.

They consist, practically, in igniting nitrogenous organic substances in the presence of potassium carbonate and charcoal. Under these conditions (without entering at present into the discussion of the reactions which take place in this formation) there is formed potassium ferrocyanide through the union of the four elements—iron, nitrogen, carbon, and potassium:



The discovery of ferrocyanide proceeds from that of Prussian blue; but it came about much later. It is known that Prussian blue, discovered by Dippel, was prepared by the ignition of dried beef-blood in the presence of potassium carbonate, the mass thus obtained, on treatment with water, giving a solution known as "blood-lye," which when treated with an iron salt yielded Prussian blue. For a long time the composition of "blood-lyes" was unknown.

In 1752, Macquer succeeded in regenerating this product by treating Prussian blue with an alkali, and his ideas concerning the nature of this reaction led him to give it the name of phlogisticated alkali.

Toward 1780, Sage, and later Bergmann, successively established that these "blood-lyes" yielded on concentration and crystallization a definite body, to which they gave the name of "blood-lye" salt, a name which it held for a long time.

It was not until 1823, thanks to the remarkable researches of Gay-Lussac, that the composition of this salt was known, which is ferrocyanide or cyanoferride of potassium, more commonly called



yellow prussiate of potash. Such was the beginning of its manufacture.

As a rule, all nitrogenous organic substances, whether of vegetable or of animal origin, may be utilized for the preparation of ferrocyanide. But, as has already been remarked, these substances almost always possess a considerable value because they may be employed either in feeding or in domestic economy. They are too expensive. Therefore the yellow prussiate industry makes use of the residues or waste products the value of which is much less.

We have seen that at first dried beef-blood was used. In 1724 Brown proposed to substitute for it meat, and finally in 1725, Geffroy made use of wool wastes and hartshorns.

The organic substances used in the manufacture of yellow prussiate may be divided into five classes: hair, rags, horn, leather, and tendons.

Under the term horn are included hoofs, the claws of animals, points of horns, defective horns, the wastes from the manufacture of combs, buttons, etc.

Hair and rags, which are often put in the same class, include bristles of swine and hair unfit for the manufacture of the various kinds of brushes, wool wastes, the hair of domestic animals, the wastes of woollen cloth which cannot be used in paper-making, damaged cloth, and the trash obtained in trimming cloth, generally called shearings.

Leather may be divided into two groups:

(1) The wastes or clippings of new leather, i.e., the wastes of harness-shops, morocco-leather manufactories, shoe-shops, tanneries.

(2) Old leather, more commonly called old shoes.

Red leather is to be preferred, chamois leather is rarely used, and white leather never. The wastes of kid-glove manufactories cannot be used on account of the presence of alum.

By tendons it is understood the slaughter-house detritus, certain portions of dead animals, and the dried muscles of these same animals.

The composition of these different products depends upon the circumstances inherent in the treatment to which they have been subjected, or upon the condition in which they have been found.

Three essential elements must be taken into consideration in

the substances used for the manufacture of ferrocyanide, viz., the percentage of nitrogen, of sulphur, and the amount of ash.

Upon the richness in nitrogen depends the value of these substances and therefore the yield in prussiate. This is therefore of first importance. As to the other two elements, they are interesting only so far as they exert a detrimental action on the yield.

In fact, in proportion as these two elements are present is the percentage of nitrogen less. Moreover, the sulphur may unite and form sulphocyanide, which reduces by so much the yield of ferrocyanide. This objection may be avoided by adding iron to the mass; the iron sulphide formed will be converted into ferrocyanide when the mass is lixiviated. The composition of the ash should be taken into consideration; phosphoric acid and silica exert a detrimental action on the formation and crystallization of ferrocyanide.

The following table gives the composition of the nitrogenous organic substances most generally used in the manufacture of ferrocyanide.

It should be mentioned, as will be seen on examining the table, that the organic substances contain three times as much, and sometimes more, carbon as nitrogen, while yellow prussiate contains these two elements in about equal proportions (116 of carbon, 120 of nitrogen).

The nitrogenous organic substances, when subjected to ignition, lose  $\frac{1}{4}$  of their nitrogen in the form of ammonia or ammoniacal compounds at a temperature below that of the formation of cyanide.

Thus, these substances are often subjected to a previous ignition at a low heat, during which the ammoniacal products set free are collected. The residue is animal charcoal, containing the rest of the nitrogen. The percentage of nitrogen itself varies, depending upon the process of ignition, the percentage decreasing with the increase of temperature of ignition. In general one seeks to produce a charcoal containing 4–5% nitrogen, which corresponds to about a  $\frac{1}{3}$  diminution of the mass.

This ignition takes place in cast-iron boilers 1 meter high and 1 meter in diameter the cover of which is provided with an exit tube connected with an apparatus which serves for the absorption of the ammoniacal compounds. Since the bottom wears away so rapidly it is so arranged that it may easily be replaced.

Name.	Nitrogen.			The Ratio of Nitrogen to Animal Matter.	Sulphur, Per Cent.*	Ash, Per Cent.†	Per Cent Composition of Ash.†		
	Payen and Boussingault.	Nitlner.	Karmrodt.				Soluble Alkali Salts.	Phosphoric Acid.	Silica.
Horn—not dried. . . . .	14.4	10.5	15 to 17	10.5 to 17					
" " dried. . . . .						1.00	20.07	52.68	27.25
Horn points. . . . .					1.37 to 1.51				
Beef hoofs. . . . .					1.12 to 1.28	3.71	13.94	43.30	42.76
Sheep hoofs. . . . .					3.00 to 3.08				
Beef horns. . . . .						0.88	35.50	39.60	24.90
Refuse in manufacture of combs. . . . .									
Dried beef-blood. . . . .		15 to 16	15 to 17	15 to 17					
Decanted and pressed beef-blood. . . . .		15 to 16	15 to 17	10 to 16					
Good. . . . .	16.0	10	16	10 to 16					
Poor. . . . .	16.0	10	10						
Sorted. . . . .						9.57	18.85	41.45	39.70
Unsorted. . . . .						10.73	19.00	41.50	39.50
Woolen shearings. . . . .			16 to 17	16 to 17					
Wool. . . . .					0.81 to 0.92				
Bristles of swine. . . . .						5.76	12.10	34.80	53.10
Hair of calves. . . . .						7.02	26.35	58.35	15.80
" " cattle. . . . .			15 to 17	15 to 17					
Manes of horses. . . . .					3.30 to 4.01				
Old leather. . . . .	9.3	6.7	6 to 7	6 to 9.3					
Scrapings of hides. . . . .			4.5 to 5.0	4.5 to 5.0		6.44	27.60	56.35	16.05
" " leather. . . . .									

\* By Bibra.

† By Karmrodt.

The second raw material in the manufacture of yellow prussiate is potash. Generally commercial potassium carbonate is used, which often contains other salts such as sulphate, silicate, chloride of potassium, and sometimes sodium salts. The chlorides exert no influence; the sulphates form sulphides during the process, which attack the cast metal and rapidly puts the apparatus out of service. The silicates and earthy substances likewise exert an injurious action.

One may likewise use blue potash extracted from the mother-liquors of a previous manufacture, a product which contains 40–90% potash, but 4–8% potassium sulphide, 7–16% potassium silicate, 7–13% potassium chloride. It is therefore necessary to subject these substances occasionally to purification, for their coefficient of impurities increases with the successive number of ignitions.

The iron, which is often added to the ignition, may be used in the metallic form (nails, filings, wastes from tin-plate), or oxid (forge scales), which becomes reduced at the beginning of the ignition. The forge scales are often objectionable because they contain a large amount of combined silica, and earthy matters.

The manufacture of potassium ferrocyanide comprises three distinct stages:

1. Ignition or production of the metal.
2. Lixiviation of the metal.
3. Crystallization.

**1. Ignition or Production of the Metal.**—By the name metal is meant the crude product resulting from the ignition of the nitrogenous organic substances in the presence of iron and alkali.

The amount of these raw materials to be used is as follows:

Carbonate of alkali. ....	100	parts
Nitrogenous substances (130–140 at a maximum, 170 with animal black).....	125	“
Metallic iron. ....	6 or 7	“

The whole mixture of these substances may be charged in retorts or ovens, but it is much better first to add the potash, then to shovel in the animal substances.

In fact, under the influence of the high temperature necessary to carry on the reaction, an abundant liberation of combustible gases is produced (carbon monoxid, carbides, carbonic acid), which

remove from the mass a large amount of heat. The successive additions of animal substances to the mass restore to it the amount of heat lost. To carry on the reaction in the best way, it is necessary that the temperature be always sufficiently high that the alkali carbonate may be reduced by the charcoal, but it should not be too high, otherwise some of the cyanide formed will be volatilized.

The operation takes place in iron kettles, or in specially constructed retorts, or in reverberatory furnaces.

The oldest apparatus known is pear-shape (Fig. 17). This oval or pear-shaped retort (*A*) is of iron and rests on one side, on

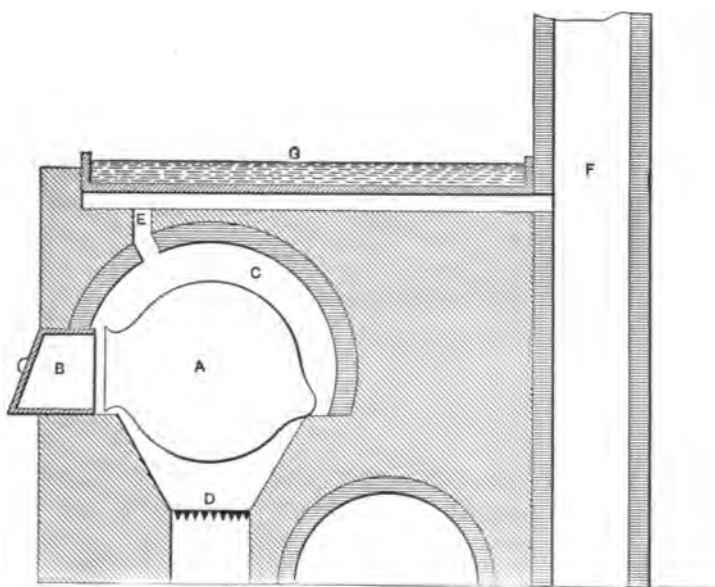


FIG. 17.—Pear-shaped Retort for the Manufacture of Ferrocyanide.

*A*, retort; *D*, fire-grate; *C*, vault; *E*, flue for the outlet of gases; *B*, opening for charging and unloading; *G*, kettle for the evaporation of the strong solutions.

the stonework of the oven, by means of a powerful trunnion, and on the other, on the façade wall of the oven by its neck. It thus presents a slight inclination backward. It is 1.20 meters long, 0.80 meter in diameter, and 0.15 meter thick. The rounded part of the retort is free, and is completely exposed to the action of the flame which arises from the grate *D*. The opening *B*, which

serves to load and unload the retort, is closed by a sheet-iron lid. The products of combustion, coming from the fire-grate *D*, are distributed on each side of the retort, and again come together in the arch *C* and escape by means of the flues *E*. The heat lost from these gases is utilized in evaporating the strong solutions in the vessel *G*. The retort *A* may be turned over from time to time in order to change the surface coming in direct contact with the flame and to avoid a too rapid wear and tear. There are two objec-

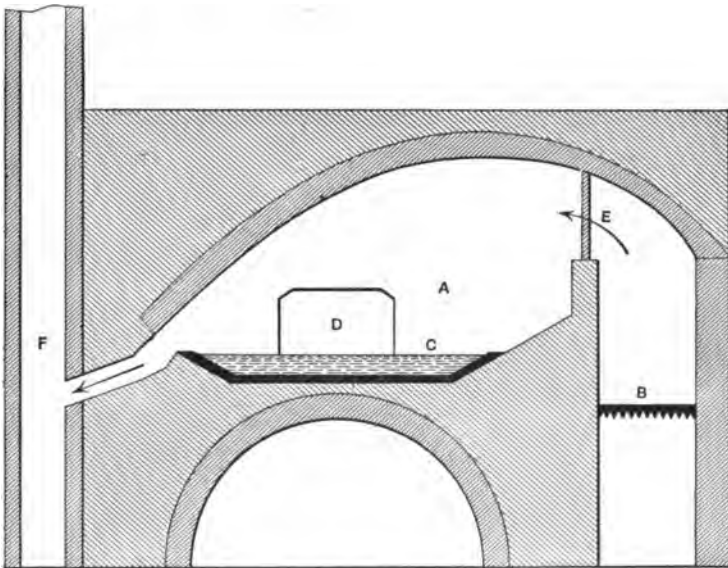


FIG. 18.—Reverberatory Furnace.

tions to this class of apparatus: they wear out very rapidly, and the action of the heat may be exerted on the substances only through the walls of the retort.

The pear-shaped retort has been replaced by the reverberatory furnace. The sole of this furnace consists of a cast-iron cupel *C* (Fig. 18) 1.1 meters in diameter and 0.10 meter thick. The fuel is put on the grate *B*, the products of combustion follow the conduit *E* in the direction indicated by the arrow, and come to the vault *A*, where they heat the cyaniding mixture from above, and in this way the high temperature necessary for the reaction is more easily attained.

In some works the gases of the grate pass under the cupel before coming in contact with the surface of the mixture. On coming out of the vault *A* the gases pass through a lateral tube and thence through the chimney *F*, whence they are conducted under evaporating-kettles which they heat.

In these furnaces 500 kg. of material may be converted at one time into yellow prussiate. The cupels wear out rapidly, but can easily be replaced; thus, after 700 tappings, a 1500 kg. cupel will weigh no more than 250 kg., and should not be used further. The wear and tear is particularly rapid in the case of furnaces with double circulation, where the combustion gases pass above and below the cupel. These furnaces have been used quite extensively in Germany.

The operation is as follows: The cupel is first heated to redness. When this is done, the inlet of gases is shut off and the mixture of potassium carbonate and blue potash is introduced into the cupel, and the cover closed. The gases are let on again and the mass brought to fusion. When this is in perfect fusion, the poker is introduced and the nitrogenous substances shovelled in, mixing them in the mass with the aid of the fire-iron. A lively reaction takes place, accompanied by effervescence and an abundant liberation of combustible gases which burn at the surface of the bath with flames sometimes, 2 meters in length.

To prevent the fused mass from overflowing, small portions of nitrogenous substances are added whenever the reaction becomes too lively. When about half of the nitrogenous substances has been added, the reaction becomes more gentle; further addition is stopped for  $1\frac{1}{2}$ – $3\frac{1}{4}$  of an hour, during which time the mass is vigorously stirred with the poker until the bath is completely fluid. The rest of the organic substance is then added in 2 or 3 portions. All these operations require about 2 hours. The mass is again heated for  $1\frac{1}{2}$  hour, after which it has the appearance of a thick liquid, and is run into moulds with the help of an iron spoon. After cooling, it has the appearance of loaves of bread. As a rule, 6 tappings of 250 kg. each may be made for each furnace every 24 hours; but, of course, the length of the operation varies according to the nature of the substances acted upon, the intensity of the fire, the experi-

ence of the workman using the poker, etc. In any case it varies from 4 to 6 hours.

In England, preference was given to vertical cast-iron boilers, slightly narrowed at the opening and provided with a mechanical stirrer whose axle penetrated the cover, and set in motion by means of gears connected with the source of power. This arrangement allowed a good deal of manual labor to be spared. Generally these boilers were arranged in series of 24.

Although this method has certain advantages, it has great disadvantages. The greatest objection consists in the losses, which are appreciable, due to the fact that the nitrogenous substances float on the surface of the bath and there burn, the nitrogenous gases liberated thereby coming in contact with but a thin layer of potash and thus escape without being combined.

Engler's process has the object in view of obviating this difficulty by causing the nitrogenous gases to become liberated in the very midst of the mass itself.

**Engler's Apparatus.**—This consists of a vertical boiler 60 centimeters in diameter and 2 meters high. A piston, formed by a perforated sheet-iron disc and moved to and fro, continually rams the nitrogenous substances into the very mass itself. First, 300 kilograms of potassium carbonate are placed in the boiler; when this is melted small portions at a time of nitrogenous substances are added through the hopper (the piston being lowered), till the whole of the nitrogenous substances has been added. The unloading is done from beneath, and the mass is collected in a suitable truck. The ammonia set free during the reaction is collected in a tower filled with pieces of coke.

The product of ignition obtained in either one of the processes just described is a greenish-black mass, quite hard, porous, absorbing atmospheric moisture energetically, with liberation of ammonia and hydrocyanic acid. This is the mass which is commonly called *metal*. It yields about 16% potassium ferrocyanide. Its composition varies, of course, with the composition of the substances used, the length of the operation, and the method used in carrying it on.

Karmrodt, who took the average of ten tappings, produced by igniting 100 parts of potash, 100 parts nitrogenous material, and 10 of iron, gives the following figures:



Cyanide of potash.....	8.20
Sulphocyanide of potassium.....	3.33
Cyanate of potassium.....	2.46
Carbonates of sodium and potassium.....	57.56
Sulphate of potassium.....	2.82
Silica.....	3.10
Insoluble.....	18.11
Undetermined.....	4.42
	<hr/>
	100.00

As may be seen, the metal does not contain any ferrocyanide. This salt is formed only on lixiviation.

The metal is broken into lumps as large as one's fist and thrown into vats containing water or weak solutions from a previous operation; this is heated to 60–90° for 12 to 14 hours while stirring. The temperature should not exceed 90°, nor be kept at that point too long, for the cyanide might be converted into ammonia and potassium formate.

When all the solid pieces have disappeared and the solution shows about 24° B., it is allowed to stand 3 or 4 hours, after which the clear liquid is decanted. The residue is washed with fresh water, the washings being used in lixiviating the succeeding metal.

The clear liquid or "blood-lye," which is greenish black in color, is concentrated in kettles by the waste heat from the ignition furnaces until the solution shows 32° B. It is finally run into wooden crystallizing vats, where it deposits on cooling a grayish crystalline product, called crude salt, containing about  $\frac{1}{6}$  of its weight of ferrocyanide of potassium.

This crude salt is withdrawn and placed in wicker-baskets in order to drip. It is purified by a second and sometimes a third crystallization. The final product is a lemon-colored salt—potassium ferrocyanide,  $\text{Fe}(\text{CN})_6\text{K}_4 + 3\text{H}_2\text{O}$ .

When the mother-liquors are concentrated to 40° B. a fresh quantity of very small crystals appears, which are purified by repeated crystallization.

Gentile avoids the second crystallization by precipitating the ferrocyanide completely from its solution at the boiling-point. The lyes at 35° B. are heated to boiling. Under these conditions the

salt is deposited; this is withdrawn and allowed to drip. When the lyes show  $50^{\circ}$  B., the boiling is stopped and the lyes allowed to stand overnight, when the rest of the cyanide is deposited. In this way no very small or "fat" crystals are obtained; the mother-liquors are treated directly in order to obtain the blue potash. Gentile's method of obtaining the crude salt yields somewhat more potassium sulphate than the ordinary method.

It remains but to purify the crude salt obtained by either of these two methods; to this end, it is dissolved in just enough hot water so that the solution shows  $32^{\circ}$  B. It is allowed to stand and is then drawn off or filtered in order to separate the black particles of insoluble residue which detract from the appearance of the product. The clear solution is then transferred to rather deep wooden or sheet-iron crystallizing vats which are surrounded by insulating bodies, where it is left during 8–10 days. The ferrocyanide is deposited, the mother-liquors being drawn off carefully and used to dissolve a fresh amount of crude salt, while the crystals are covered over with a new solution sufficiently concentrated to add to the crystals already deposited. This is repeated until the crystals obtained are 10–12 cm. in length. In fact, commerce seeks rather to have large and regular crystals than pure ones. The crystals are removed, washed with a small amount of water, and dried.

Sometimes the salt is crystallized in groups by suspending crystals to threads tied to wooden rods placed in the crystallizing-vats.

As to the very fine crystals, they are dissolved in water, and, after concentrating the solution to  $30^{\circ}$  B., allowed to crystallize; the salt thus obtained is added to the crude salt and treated as such. The mother liquors, evaporated to  $40^{\circ}$  B., yield pearly crystals of a double salt of cyanide and chloride of potassium, much used in the manufacture of alum.

The refined salt is never pure: it always contains a little potassium sulphate which is difficult to get rid of. Yet one may obtain it free from sulphate by dissolving the salt in water and concentrating the solution to the density 1.31. At this point the greater part of the sulphate of potash separates out. Water is then added to bring the density to 1.27 and the solution allowed to crystallize. This is done but rarely, for the presence of potassium sulphate does

not in any way interfere with the industrial use of potassium ferrocyanide, the only objection being that it reduces by just so much the amount of useful cyanogen.

The manufacture of potassium ferrocyanide leaves behind two important residues: a black mass and blue potash.

The black mass is made up of the residue from lixiviating the metal. It is friable and of a composition varying according to the nature of the organic substances used and the method of procedure. It consists to a large extent of carbon and mineral substances—silicates, phosphates, chlorides, sulphides, soda, potash, lime, etc.

In the following table Karmrodt gives the analyses of three samples of this black mass:

Substance.	Horn.	Leather.	Rags.
	Per Cent.	Per Cent.	Per Cent.
Charcoal . . . . .	6.10	9.19	4.22
Potash . . . . .	12.18	10.22	16.70
Lime . . . . .	16.20	19.66	18.45
Magnesia . . . . .	2.15	0.97	1.27
Sesquioxid and metallic iron . . . . .	16.14	3.10	2.12
Alumina . . . . .	4.80	14.17	10.24
Manganese . . . . .	0.42	0.72	0.06 (?)
Copper . . . . .	trace	0.02 (?)	0.42
Silica . . . . .	21.14	26.45	29.70
Sulphuric acid . . . . .	1.27	1.85	0.16
Phosphoric acid . . . . .	10.45	4.92	6.44
Residue: Sulphur, CO <sub>2</sub> ; chlorine, CN	9.15	8.73	10.22
	100.00	100.00	100.00

The amount of the black mass varies according to the substances used. Karmrodt found the following:

Using wool wastes . . . . .	28.3%
“ horn . . . . .	18.7
“ hair . . . . .	23.0
“ leather scraps . . . . .	35.0

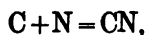
It is sold mostly as a fertilizer, due to its high content of potash and phosphoric acid. In order to recover the potash (9%), various uses have been attempted, especially that of utilizing it in the manufacture of alum, but the experiments thus undertaken were not successful owing to the fact that the labor cost more than the value of the product.

Blue potash is the residue after evaporating to dryness the mother-liquors obtained from the crystallization of the crude salt. It contains potash in excess in the free state or in the form of salts not combined with cyanogen, and the salts supplied by the ash. It is used again in the process, mixed with fresh potash. Its composition varies according to the number of ignitions to which it has been subjected. It is evident that it becomes more and more impure, and ends by becoming useless.

	Hoffmann.	Brunquell.	Karmrodt.
Potassium carbonate. . .	44.1 to 84.0	71.9	52.75
“ silicate. . . . .	7.6 to 20.4	11.9	16.57
Sulphide . . . . .	1.4 to 8.8	4.3	6.18
Chloride. . . . .	7.2 to 13.1	.....	1.15
Phosphate. . . . .	.....	.....	2.04
Sulphate. . . . .	.....	.....	4.34
Potash . . . . .	.....	.....	7.22
Ferrocyanide. . . . .	.....	.....	2.84
Sulphocyanide. . . . .	.....	.....	trace
Insoluble residue. . . . .	} 26.77 {	1.6	3.86
Other substances. . . . .		8.2	3.07
Water. . . . .		2.1	

**Theory of the Manufacture of Potassium Ferrocyanide by the Old Process.**—Several hypotheses have been proposed on this subject, the first and most probable of which is the following:

Nitrogenous organic substances contain carbon, nitrogen, hydrogen, and oxygen. After ignition, they still contain all these elements except oxygen and a large part of the nitrogen which is volatilized in the form of ammonia. Now as the amount of carbon in these substances is much larger than that of nitrogen, it follows that only a part of this carbon enters into combination with the nitrogen in order to yield cyanogen,



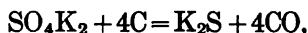
and the rest of the carbon reacts upon the carbonate of potash, which it reduces, thus setting the metal free,



which metal, reacting upon the cyanogen formed, unites with it and produces potassium cyanide,

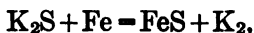


As may be seen, iron seems to take no part in this reaction, and yet it is indispensable that some be put in. In fact, carbonate of potash always contains, besides other impurities, a small amount of sulphate of potash. In contact with carbon, this salt becomes likewise reduced, yielding potassium sulphide,

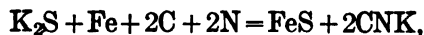


and this sulphide, in the presence of the cyanide formed, yields sulphocyanide.

The object of the iron is, therefore, to absorb the sulphur of the potassium sulphide, forming insoluble iron sulphide,



or



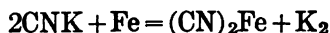
which entirely prevents the formation of sulphocyanide, the formation of which must, under all circumstances, be avoided in the manufacture of potassium ferrocyanide.

Therefore the product after igniting the raw materials (nitrogenous substances, carbonate of potash, iron), otherwise called the metal, will be a rather complex mixture which may contain:

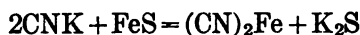
Potassium cyanide;  
Alkali carbonate in excess;  
Undecomposed organic substances;  
Iron;  
Iron sulphide;  
Carbon.

It should be stated that we do not include the presence of potassium ferrocyanide in the said mixture. It is, in fact, admitted, according to actual data, that this salt is formed only at the time of lixiviation in the following way:

During lixiviation, potassium cyanide reacts with sulphide of iron, yielding potassium ferrocyanide according to either of the following reactions:



or

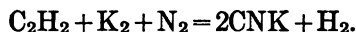


or



That is precisely the reason why one should not think of extracting directly by lixiviation the potassium cyanide formed in the "metal."

Still another theory is the following:\*. The reason for igniting organic substances is to produce a nitrogenous charcoal which would react with the potassium carbonate, yielding, in all probability, acetylene. In its turn the acetylene would react with the potassium, set free from potassium carbonate, and with the nitrogen of the organic substance, or, in case of need, with nitrogen of air, thus yielding potassium cyanide, as follows:



It is just at this point that the presence of iron would cause the formation, first of cyanide of iron, then of potassium ferrocyanide, according to the reactions above indicated.

**Yield.**—The yield obtained by igniting nitrogenous organic substances depends on several conditions.

From many experiments on a large scale made by Karmrodt, it follows that the yield may vary from 10–18% of the weight of the salt used.

As an average of 459 different operations, Fleck places the yield at 11%.

Hoffmann studied the various conditions which may influence the yield, the following being the result of his investigations:

- (1) The nature of the nitrogenous organic substances exerts a

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\* Prunier, *Médicaments chimiques*, Vol. I.

considerable influence on the yield of cyanide and of sulphocyanide; it is, however, impossible to establish a fixed relation between the yield and the nitrogenous content of the organic substances used.

(2) The formation of potassium cyanide is quite closely proportional to the weight of organic substances.

(3) The yield seems to increase with the purity of the alkali.

(4) The yield increases especially with the temperature.

(5) It increases more rapidly still if for a like quantity of potash the addition of organic substances be increased.

(6) If blue potash be employed, the amount of black mass is twice as great as if pure potash had been used.

(7) For the same amount of potassium ferrocyanide produced, the amount of pure potash consumed depends on the nature of the organic substances.

(8) The consumption of organic substances is greater with blue potash than with pure potash.

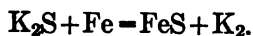
(9) The amount of sulphocyanide formed does not vary whether iron shavings or iron turnings be added to the mixture; but it decreases if finely divided reduced iron be used; there is almost no formation if at the end of the operation forge scales be added. To these theoretical considerations should be added the following, based upon experimental data:

(1) A relatively small proportion ( $\frac{1}{5}$ – $\frac{1}{7}$ ) of the total nitrogen of the organic substances contributes to the formation of the cyanide. The remaining  $\frac{4}{5}$  or  $\frac{6}{7}$  are lost or volatilized as ammonia. A certain amount is, however, retained. At the beginning of ignition, the temperature being relatively low, a portion of the nitrogen escapes under the form of ammonia; but when the temperature has become raised, this ammonia coming in contact with carbon becomes converted into hydrogen and hydrocyanic acid, which latter unites with potassium in order to form cyanide of potassium. It follows that if this high temperature could be obtained from the beginning of the operation, there would probably be formation of cyanide from the first.

(2) Just as only a small proportion of the total nitrogen becomes really utilized, so only a fraction of the potash used unites with the cyanogen. According to Karmrod's experiments, this amounts to  $\frac{1}{7}$ – $\frac{1}{10}$ . It should, however, be remarked that besides

its rôle of absorbing the cyanogen formed, potash also acts as a flux, the effect of which is to reduce the mass to a state of liquid which is absolutely indispensable for the proper formation of potassium cyanide. Part of the potash is recovered in the mother-liquors, but a rather large amount is volatilized or lost in the various manipulations. According to Hoffmann this loss may amount to 10-20%.

(3) Besides cyanide of potassium there is also formed during ignition sulphocyanide of potassium. The formation of this salt is variously explained. According to some it is due to the presence of potassium sulphate in the carbonate used. Hoffmann objects to his hypothesis because when in his experiments he used potash absolutely free from sulphate, he noticed a formation of sulphocyanide to about the same extent. These investigations led to a second hypothesis: the influence of the sulphur, which is present almost always in animal substances, the amount reaching sometimes 3%. A great portion of this sulphur is, however, volatilized, the rest being converted into sulphocyanide. In fact this formation of sulphocyanide constitutes a loss from the point of view of the yield of ferrocyanide, a loss which may amount to  $\frac{1}{5}$  of its weight. It is for the purpose of overcoming this objection that iron is added, which during the fusion reduces the sulphocyanide. If, however, one succeeds in the laboratory in obtaining a metal free from sulphocyanide, it is entirely different on an industrial scale, in which case a small amount of this salt is always found. Nöller recommended the use of chalk, but the results obtained with this reagent are not very satisfactory. Forge scales give excellent results, but they have the great objection of breaking up a portion of the potassium cyanide. All in all, iron is the best reagent; it also serves in preventing a too rapid wear and tear of the apparatus; it unites with the potassium sulphide and converts it into iron sulphide, which does not attack the walls of the vessels.



(4) The reaction should not be carried on too far, otherwise the yield may decrease 9-12% (Hoffmann).

(5) The substances employed should all be absolutely dry, the water-vapor set free during the reaction exerting an action which decomposes the cyanide formed.



**Observations Concerning Lixiviation and Crystallization.**—(1) The use of iron protoxid salts to convert cyanide into ferrocyanide is advantageous. The carbonate or sulphate of iron may be used, but generally in the industries the use of sulphide of iron is preferred.

(2) In evaporating the lyes, it is best not to bring them immediately to the boiling-point, otherwise the unconverted cyanide of potassium would be decomposed. The temperature should not exceed 70–80°. Brunquell recommends macerating the metal during 24 hours at 50–60°.

The sum total of these various theoretical and practical considerations shows well that the manufacture of potassium ferrocyanide by the old process is filled with defects and requires a great deal of care if a really profitable yield is to be obtained. All in all, the losses are considerable and intimately bound to numerous circumstances. The chief objections to this method may be thus summed up:

(1) Serious losses of nitrogen through volatilization at the time of ignition.

(2) Loss of potash.

(3) Loss of cyanide because of the formation of sulphocyanide and cyanate.

(4) Loss of cyanide due to the incomplete transformation of this salt at the time of lixiviation.

(5) Rapid wear and tear of the apparatus.

(6) Heavy expense for fuel.

It has been sought to remedy these objections, and numerous improvements have been applied to the methods which we have just described.

The object of most of them is to utilize, as much as possible, the nitrogen, which at the beginning of ignition escapes from the organic substances under the form of ammonia. Such are the processes of Brunquell and of Karmrodt.

**Brunquell's Process.**—This process may be carried out in two different ways.

In the first, two iron retorts are used connected with a vertical tube. The mixture of organic substances, potash, and iron prepared in the ordinary manner is charged into the lower retort, while the upper retort contains a mixture of animal charcoal and potash.

These two retorts are placed in a specially constructed furnace. First the upper retort is heated to bright redness, and then the lower retort is so heated as to bring the mass to a state of fusion.

In Brunquell's second improvement, only one cylinder is used, the lower half of which is filled with the ordinary mixture and the upper half with charcoal and potash. This cylinder is suspended by a chain and may be raised or lowered at will into a vat-like furnace which is provided with a grate containing a hole through which the cylinder may pass. At the beginning of the operation the cylinder is lowered deep enough so that only the upper part is subjected to the heat; when this part has reached the desired temperature, the cylinder is raised so that it is found completely in the furnace and consequently heated on all sides.

In this way, in the first as well as in the second apparatus, the gases set free by the mixture of the lower part passed through the upper mixture. Notwithstanding these advantages Brunquell's two processes have never been adopted on an industrial scale.

Still another improvement, due to Brunquell, consists in converting most of the nitrogen into volatile products by means of repeated distillations with lime, then to utilize the ammoniacal products thus obtained for the manufacture of ferrocyanide by passing them through a series of cylinders filled with charcoal and potash heated to bright redness. The ammonium cyanide thus formed is collected in a strong solution of sulphate of iron. Cyanide of iron is formed, which when boiled with potash is converted into potassium ferrocyanide. For a certain time this process was tried in France, with this modification, however, that the ammonium cyanide was absorbed by a strong solution of potash to which a salt of iron had been added.

**Karmrodt's Process.**—Along the same line, Karmrodt's process should also be mentioned. The object of this process is the same as that of Brunquell, and it may profitably be combined with the manufacture of animal black. The apparatus used consists of two parts, the carbonization vessel and a cylinder charged with wood charcoal impregnated with potash. The two parts are connected by means of a tube. The cylinder, which is vertical, is provided with a fire-grate; one begins heating the cylinder by means

of this fire-grate. With the aid of a special appliance the products of combustion are conducted either into the main chimney or into a flue joined to the carbonizing retort. When the cylinder has reached the temperature of redness, the gases of the fire-grate are conducted under the carbonizing retort. The volatile products here liberated pass through the connecting tube into and through the cylinder.

The yield is appreciably greater than by the ordinary process, but it is, nevertheless, far from the theoretical yield, which the whole of the ammoniacal products set free should give.

Several processes for the conversion of sulphocyanides into ferrocyanides have been invented, among which only two deserve to be taken into consideration.

**Conroy's Process.**—The first is that of Conroy, Hurter, and Brock (1896). It consists in treating the crude sulphocyanide with a solution of ferric or ferrous chloride. The mixture is heated to 270–280°, in an autoclave provided with a stirrer, in the presence of an excess of iron, preferably reduced iron.

The sulphocyanide is converted into a mixture of ferrocyanide and sulphide of iron, which is collected, washed, and finally decomposed with a caustic alkali. The residue from the treatment with alkali, consisting of a mixture of sulphide of iron and ferric and ferrous hydrate, is treated with hydrochloric acid, which forms iron chloride, which may be used anew. The hydrogen sulphide thus liberated is collected and used.

**Musspratt's Process.**—The second process is that of H. E. Hetherington and E. K. Musspratt (English patent No. 5830, March 20, 1894).

It consists in treating a sulphocyanide of an alkali or alkaline earth with metallic iron. First finely divided iron (filings, turnings, or iron sponge) is heated with tar, the object being to reduce the oxid which always forms on the surface of these products. The iron thus prepared is mixed with sulphocyanide and tar in the following proportions:

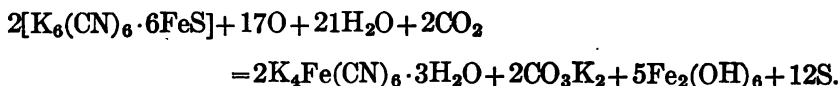
Reduced iron.. .. .	70–80 parts
Tar.. .. .	20–40 “
Sulphocyanide of potassium or sodium.. .. .	100 “

This mixture is heated to 350° F. in a closed vessel connected by a tube to a condensation retort. This retort serves in condensing the sulphocyanide which might be volatilized during the operation.

The product of the reaction consists of a mixture of alkali ferrocyanide, iron and alkali sulphides, and tarry residue. It is treated with hot water, the solution thus obtained being treated with carbonic acid, which removes the hydrogen sulphide, and then concentrated to crystallization. In case of ferrocyanide of sodium, it is best to concentrate directly.

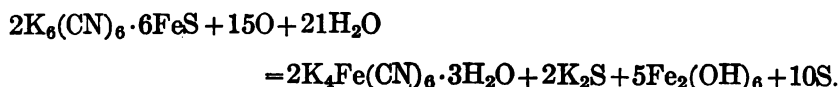
**Goerlich and Wichmann's Process.**—This process (German patent No. 9139, Aug. 4, 1894, March 11, 1895) is practically the same.

It consists in fusing alkali sulphocyanide with iron and treating the product of fusion, before lixiviation, with a current of moist air mixed with carbonic acid. In this way ferrocyanide, sulphur, alkali sulphide, and carbonate are obtained:



By this process almost the whole of the sulphur is removed, and alkali carbonate is obtained instead of alkali sulphide.

In the absence of carbonic acid, the reaction is as follows:

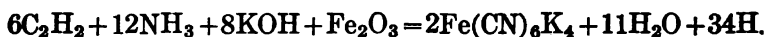


The oxidized product is treated with water, and the soluble salts are separated by fractional crystallization. The residue may be used in recovering metallic iron.

**Process of the Works du Castelet.**—Lastly, we will mention the extremely original process described in the patent No. 308808 of March 8, 1901, taken by La Société des Usines du Castelet, and Leriche.

It consists in causing a gaseous mixture of  $\frac{1}{3}$  acetylene and  $\frac{2}{3}$  ammonia to act, at a nascent red heat, upon an intimate mixture

of oxid, carbonate, or hydrate of iron and alkali oxid in a closed vessel. The reaction is as follows:



The product is dissolved in boiling water, the clear solution being decanted, evaporated, and allowed to crystallize on cooling.

## II. EXTRACTION OF CYANIDE COMPOUNDS FROM ILLUMINATING-GAS AND FROM THE BY PRODUCTS OF ITS MANUFACTURE.

The manufacture of illuminating-gas has made great strides in the last thirty years in England, Germany, and in France. Thus the annual consumption of gas in England reaches almost 3000 million cubic meters; in France it is about 700 million cubic meters.

As will be seen later, the cyanide compounds exist already formed in the gas. It is therefore quite natural that one should think of reaping some advantage from it. To be sure, the percentage is quite small, and sometimes even trifling; but on the other hand, if one thinks of the enormous quantity of gas annually produced in the different countries, one can easily conceive how the gas industry may offer a profitable source of cyanide production.

Further, it should be stated that cyanogen is an injurious product which it is necessary to remove before delivering the gas for consumption. It decreases the illuminating power perceptibly, and is a toxic product. Besides its being absolutely necessary to remove it from the gas, there is profit in its recovery.

In England the question of cyanides in the manufacture of gas has keenly prejudiced the mind, and the manufacturers and investigators have foreseen the advantage to be derived in these substances in a country so rich in coal and gas. Germany is not at all behind in this respect, there being few gas-works which do not recover the cyanide compounds.

On the other hand, France has shown but little interest in this question, and even at the present time there seems little disposition to extend this industry.

Moreover, it is a fact to be regretted that in France so little importance, and sometimes even not any at all, is attached to the by-products of certain manufactures. It is not a rare sight, indeed, to see numerous works neglecting such an interesting and often remunerative question as the recovery of by-products. Thus, for example, in the case of illuminating-gas, there are to our knowledge works of importance which do not even condescend to take the trouble to purify the gas, or if they are compelled to do this because of hygienic statutes, do not get any profit out of their sluice waters or from their spent oxid.

And yet in most cases the recovery and utilization of by-products (especially in the industry which we are discussing) require but slight costs of installation, costs which are repaid by the profits obtained and by a better quality of product, which is the chief object of the manufacturer. It should also be stated that the process of recovering these by-products does not generally modify the carrying on of the operations.

Thus, if one considers that in France the manufacture of illuminating-gas requires annually about 4,000,000 tons of coal, and that from each ton one can extract cyanide compounds worth 2-3 francs, it is easily seen that the illuminating-gas industry could recover, each year, a profit of 8 to 12 million francs, which is not at all an amount to be neglected.

One objection may be interposed to the above remarks, and that is, that in France many gas-works are of but slight importance, and under the circumstances the recovery of these by-products seems to offer no benefit considering the small amount of product to be treated. To this objection the following reply may be made: Most of the gas-works are in the hands of powerful companies often possessing a large number of works. It would be a simple matter for each works to recover the cyanide compounds, and to obtain concentrated products (e.g., masses rich in cyanide) which might be profitably transported to a central works, which could be especially occupied with the treatment of by-products furnished by all the works of the company. The expense would be slight and large profits would be assured.

From all the foregoing remarks it follows that the gas industry may with advantage prove a source of production of cyanide com-

pounds, a production which would require but little expense if it were well understood, and which under these conditions would almost suffice for the demand in the cyanides.

There is therefore, every reason, and it is also necessary, that the cyanide compounds should be recovered from the gas, and one should encourage every gas-manufacturer so to do.

We shall now study the various ways proposed to bring about this operation profitably, but before that it seems necessary to mention briefly in what the manufacture of illuminating-gas consists.

As is well known, illuminating-gas is a product of the distillation of coal in closed vessels. Coal used in the manufacture of gas is the dry smiths' coal burning with a long flame, and containing the following percentage composition (water and ash free):

O = 7.71

H = 5.40

C = 85.89

N = 1.00

---

100.00

The principal types of coal most commonly used are those from Nord, Pas-de-Calais, Mons, the Sarre, Ruhr, and Newcastle. This distillation takes place in retorts, formerly made of cast iron, but now of refractory brick, arranged ordinarily in a series of seven or nine, in a furnace which is heated either directly with coke or by means of combustible gases produced by a gas-generator placed under the furnace for the recovery of the heat. These retorts, whose dimensions vary with the size of the works, are heated to a temperature of about 1100°. The resulting gas consists of a very complex mixture of different products (volatile and non-volatile hydrocarbons, ammonia, and ammoniacal salts, hydrosulphuric and hydrocyanic acids). Thus obtained, this product is unfit for domestic use, and must therefore be subjected to purification. The object of this purification is to separate the products, which on account of their easy condensation would befoul

and obstruct the pipes, or which on account of their own characteristics would considerably decrease the illuminating power of the gas, or would constitute a source of danger to the health of the consumers on account of their noxious properties.

The purification of gas is carried on in two stages: the first is purely physical, whereas the second is based on chemical reactions.

The physical purification consists in removing all the easily liquefiable or condensable products; the chemical purification consists in absorbing all the harmful substances which escape the physical by means of certain definite substances. The method of procedure is as follows:

On emerging from the retorts the gas passes into a horizontal cylindrical apparatus half filled with water into which cylinder outlet tubes from all the retorts converge. The level of the water is kept constant by means of an overflow. The gas abandons in this apparatus the less volatile products (tars) and a portion of the ammonia. From there the gas goes to a collector, a very long horizontal tube about 0.80 metre in diameter, where a great part of the light tars that have escaped the previous treatment are deposited. Then it goes into a condenser or cooler consisting of a system of inverted U tubes, joined to a rectangular box, divided into sections by partitions, into which the condensed products are collected (water-vapor, ammoniacal salts, ammonia, and the tars which have escaped the first and second treatment). The last traces of these products are removed in the scrubber, a tall cast-iron cylinder consisting of two chambers filled with coke and into which a thin stream of water flows in a direction opposite to that of the incoming gas. Finally by passing the gas through the Pelouze and Audouin condenser the last traces of tar are removed, and it only remains to subject the gas to the second stage for chemical purification. For this purpose the gas passes into a series of boxes filled with a mixture of sawdust, ferric oxid, lime, and sulphate of lime, which absorbs the ammonia, carbonic, hydrosulphuric, hydrocyanic, sulphocyanic acids, etc. When this mixture no longer exerts any purifying action, it is "revivified" by spreading and stirring it in the air, when it may be used again.



As may be seen by this short sketch the manufacture of gas yields many different products which may be divided as follows:

## I. COKE.

## II. AMMONIACAL LIQUORS.

Principal elements	{	Ammonium carbonate.....	$(\text{NH}_4)_2\text{CO}_3$
		Ammonium sulphide.....	$(\text{NH}_4)_2\text{S}$
Minor elements	{	Ammonium chlorid.....	$\text{NH}_4\text{Cl}$
		Ammonium cyanide.....	$\text{NH}_4\text{CN}$
		Ammonium sulphocyanide.....	$\text{NH}_4\text{CNS}$

## III. ILLUMINATING-GAS.

Illuminating elements	Gas	Acetylene.....	$\text{C}_2\text{H}_2$
		Ethylene.....	$\text{C}_2\text{H}_4$
		Propylene.....	$\text{C}_3\text{H}_6$
		Butylene.....	$\text{C}_4\text{H}_8$
		Allylene.....	$\text{C}_3\text{H}_4$
		Crotonylene.....	$\text{C}_4\text{H}_6$
		Terrene.....	$\text{C}_4\text{H}_8$
		Benzol.....	$\text{C}_6\text{H}_6$
	Vapors	Thiophene.....	$\text{C}_4\text{H}_4\text{S}$
		Styrolene.....	$\text{C}_8\text{H}_8$
		Naphthalene.....	$\text{C}_{10}\text{H}_8$
		Methylnaphthalene.....	$\text{C}_{11}\text{H}_{10}$
		Acetylnaphthalene.....	$\text{C}_{11}\text{H}_{10}$
		Fluorene.....	$\text{C}_{16}\text{H}_{10}$
		Fluoranthane.....	$\text{C}_{16}\text{H}_{10}$
		Propyl.....	$\text{C}_3\text{H}_7$
		Butyl.....	$\text{C}_4\text{H}_9$
		Hydrogen.....	$\text{H}_2$
More illuminating elements	{	Methane.....	$\text{CH}_4$
		Carbon monoxid.....	$\text{CO}$
		Carbonic acid.....	$\text{CO}_2$
Elements which affect the purity of the gas	{	Ammonia.....	$\text{NH}_3$
		Cyanogen.....	$\text{CN}$
		Sulphocyanogen.....	$\text{CNS}$
		Methylcyanide.....	$\text{C}_2\text{H}_5\text{CN}$
		Hydrogen sulphide.....	$\text{H}_2\text{S}$
		Sulphide of carbon.....	$\text{CS}_2$
		Sulphides of the hydrocarbons.....	—
		Oxysulphide of carbon.....	$\text{COS}$
		Nitrogen.....	$\text{N}$

## IV. TAR

## V. PURIFYING MATERIALS.

Varying in composition according to the nature of the mixture used, but generally containing:

Sulphate of ammonia,  
*Ferrocyanide of ammonia*,  
*Sulphocyanide of ammonia*,  
*Cyanide of ammonia*,  
*Prussian blue*,  
 Sulphide of iron,  
 Sulphur,  
 Oxid of iron,  
 Sawdust, tar, etc.

The amounts vary according to the kind of coal used, but, as a rule, from 100 klgm. of coal the following are obtained:

I. Coke.....	70 klgm. = 1.8 hectoliters
II. Gas.....	30 cu. m. D=0.4
III. Tar.....	3½ to 6 klgm. D=1.2
IV. Ammoniacal liquors. ....	6-9 klgm. 1 to 8° Baumé (corresponding to 1-5% pure ammonia)

Of these various products three only are of interest, because they contain cyanide compounds, namely:

1. Gas itself.
2. Ammoniacal liquors.
3. Purifying materials.

We shall take up these three substances one after the other, in order to extract from the products of the distillation of coal the cyanide derivatives which they may contain, and which quite naturally vary according to the nature and the composition of the raw material used, and according to the methods of conducting the distillation.

But before taking up the extraction of cyanides in the manufacture of gas it would seem indispensable to review the various theories set forth concerning the formation of these compounds and the reactions which may produce them.

Cyanide compounds are naturally formed in the production of illuminating-gas, and they may be found, in the various stages of the manufacture, in the following forms: Cyanogen, sulphoc-

anogen, sulphocyanic acid, hydrocyanic acid, cyanide, ferrocyanide, sulphocyanide of ammonium, etc.

The nitrogen necessary for the formation of these compounds comes from the coal, which, according to the character of the coal used, contains various amounts.

Kind of Coal.	Per Cent N.	Analyst.
<b>FRENCH COALS.</b>		
Haut-fleau ("fat")	1.15	de Marsilly
Escouffiaux	1.25	"
Agrappe	1.375	"
Bracquignies ("half-fat")	1.00	"
Mariemont	0.75	"
Valenciennes ("fat")	1.65	"
Bruay	1.875	"
Noeux	1.525	"
Bully	1.34	—
Liévin	1.57	—
Bousquet d'Orb	1.40	—
Sables (washed)	1.67	—
Trélys	0.96	—
Trélys (crude)	0.63	—
Martinet (washed)	1.31	—
Fontanes	0.67	—
Givors	1.65	Ch. Méné
Rouchamp, 1.	1.09	Scheurer-Kestner
" 2.	1.06	"
" 3.	1.00	"
<b>CHARLEROI BASIN.</b>		
Poirier ("fat")	1.375	de Marsilly
Carabinier (French)	1.00	"
Bois d'Heignes	0.40	"
<b>ENGLISH COALS.</b>		
Three-quarter vein	1.65	Percy
Beg. vein	1.47	(Lab'y of Mines, London)
Low	2.05	"
Wolverhampton	1.84	"
Doul in (South), Wales	1.28	"
Newcastle	1.32	"
Glamorgan	1.69	"
Northumberland	2.05	Scheurer-Kestner
"	2.37	Ch. Méné
South of Wales coal	1.65	—
" " " "	1.49	—
Lancashire (uninflamable)	1.93	—
Scotland	2.09	—
" " " "	1.33	—
" " " "	1.57	—
" "speakcoal"	1.20	—
Cannel-coal-Wigan (Lancashire)	2.12	—
" " " " Tyneside (Newcastle)	1.85	—
Anthracite (South Wales)	0.83	—
Boghead	0.96	Genny
" " " "	0.78	Matter

Kind of Coal.	Per Cent N.	Analyst.
<b>GERMAN COALS.</b>		
Duttweiler (Saarbrück).....	0.50	Scheurer-Kestner
Altenwald ".....	0.50	—
Hernitz ".....	0.50	—
Friedrichsthal ".....	0.50	—
Louisenthal ".....	0.50	—
Königshütte (Prussia).....	0.59	Schwachhöfer
Morgenstern ".....	0.41	—
Hermenegilde (Low. Silesia).....	0.18	—
Carolinen (Prussia).....	0.24	—
Jaklowetz (Low. Silesia).....	0.20	—
Waterloo (Prussia).....	0.40	—
Altendorf.....	1.00	Scheurer-Kestner
Consolidation.....	1.50	—
Boldon.....	1.45	—
Bohemian.....	1.87	—
Zwickau.....	1.20	—
Saar.....	1.06	—

From the foregoing table, the average content of nitrogen in coal may be seen to be 1 to 1.6%.

The distillation of coal distributes this nitrogen among the various products formed, and only a small proportion passes into the state of cyanide compounds.

Forster studied the migration of nitrogen produced during the distillation of coal in closed vessels (Journal of Gas Lighting, 1882). One of his experiments was made with a coal containing 1.73% nitrogen; and this he found distributed as follows:

0.251 or 14.50% passes into ammonia

0.027 or 1.56% " " cyanogen

0.863 or 49.90% remains in the coke [state

0.589 or 34.04% passes into the tars, and into the gas in a gaseous

1.73      100.00

Knublauch, who repeated the same experiment on three samples of coal, found:

	1.	2.	3.
Total nitrogen of the coal.....	1.555	1.479	1.176
Nitrogen in the coke.....	0.466	0.526	0.751
Nitrogen in the gas.....	0.856	0.696	0.189
Nitrogen in the form of ammonia.....	0.185	0.208	0.187
Nitrogen " " " " cyanogen.....	0.0268	0.0278	0.018
Nitrogen in the tars.....	0.0212	0.0212	—
	<u>1.555</u>	<u>1.479</u>	<u>1.176</u>

Or for every 100 parts of nitrogen contained in the coal, there are

	1.	2.	3.
Nitrogen in the coke.....	30.0	35.6	63.9
“ “ “ gas.....	55.0	47.1	21.1
“ “ “ form of ammonia.....	11.9	14.1	11.6
“ “ “ “ “ cyanogen.....	1.8	1.8	1.8
“ “ “ tar.....	1.3	1.4	1.3
	<u>100.0</u>	<u>100.0</u>	<u>100.0</u>

Leybolt (*Journal für Gasbeleuchtung*, 1890) gives the following results:

Coke.....	31. to 36. %
Ammonia.....	10. to 14. %
Cyanogen.....	1.5 to 2. %
Tar.....	1.0 to 1.3%
Gas.....	46.0 to 56.0%

Guégen (*Journal du gaz et de l'électricité* 1884) likewise studied the distribution of the nitrogen in the products of the distillation of two coals, carried on at 900° in sandstone retorts.

	1. Coal from Grand-Buisson, Mons, Belgium.	2. Coal from Liévin.
Distribution of 100 Parts Nitrogen.		
Nitrogen in the form of ammonia.....	34	19
Nitrogen in the form of cyanogen in the tar and in the gaseous products.....	27	29
Nitrogen in the coke.....	39	52
	<u>100</u>	<u>100</u>

These figures are not at all absolute: they vary with the nature of the coal, the method of operation in the works, the temperature of the distillation, etc., yet they show that the amount of cyanide compounds formed is relatively small, and that it can only become of value when large quantities of coal are treated.

Cyanogen is therefore always formed in very small quantities in the distillation of coal. The amount formed depends much on the temperature of the distillation, cyanogen not being formed except in brisk distillations carried on at a high temperature. In distilling coal at a higher temperature, Foulis of Glasgow found that 2831 liters of gas yielded 6.5 grams of cyanogen, while when working at a low temperature this amount was cut down to less than half. According to Hunt, the most favorable temperature is 950° and above, while at 700 to 800° one would obtain only one twelfth as much cyanogen. This remark is, moreover, confirmed by the experimental fact that the greatest part of the cyanogen is formed toward the end of the distillation—that is, at the moment when the temperature is the highest, and at this very moment the quantity of ammonia formed is very small.

A small yield of cyanogen therefore accompanies a large yield of ammonia, and vice versa.

Perthuis carried out a series of experiments which show this to be true, and that the yield of cyanogen reaches its maximum at the end of the distillation, while at the beginning it is almost nothing:

Length of Distillation.	Hydrocyanic Acid Retained by 100 Cu. M. of Gas.
1-2 hours .....	trace
3-4 “ .....	77.1 grams
5-6 “ .....	142.1 “

The form in which the cyanogen comes out of the distillation retorts has given rise to many discussions, and the opinions expressed relative to this subject vary greatly.

According to some investigators, cyanogen occurs in the gas in the form of cyanide and sulphocyanide of ammonium.

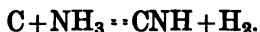
The reaction would be that indicated by Kuhlmann:



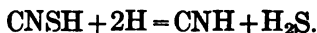
When this ammonium cyanide comes in contact with sulphur and sulphide of carbon in the highly heated retort it becomes partially transformed into ammonium sulphocyanide.

But, on the other hand, the experiments of Bergmann clearly prove that the action of ammonia on carbon or on carbon monoxid

at a red heat does not yield ammonium cyanide, but hydrocyanic acid, according to the reaction



According to Lewis, and this is the most probable opinion, the cyanogen found in gas may exist therein only in the form of free cyanogen or free hydrocyanic acid. Lewis bases his views upon the following principles: (1) It is impossible that cyanogen should exist in the gas in the form of sulphocyanic acid (CNSH), for this latter in the presence of hydrogen becomes decomposed into hydrocyanic acid and hydrogen sulphide:



(2) Neither can it exist under the form of ammonium cyanide, since this salt is decomposed from the time the temperature exceeds 26.6° C.

(3) It is also quite improbable that it occurs therein in the state of ammonium sulphocyanide, experiments having clearly proven this.

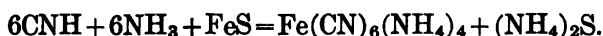
Finally, other investigators admit that ammonium cyanide is formed, but that it becomes decomposed by carbonic acid contained in the gas, this decomposition yielding hydrocyanic acid and ammonium carbonate. This would of course explain the absence of ammonium cyanide in the scrubbers.

However that may be the formation of cyanogen compounds in gas takes place in the distillation retorts at a high temperature; it probably results from the action of ammonia on carbon or on carbon monoxid at a high temperature. This reaction in all probability causes the formation of free hydrocyanic acid, which in the course of its passage through the series of apparatus becomes transformed, as will be seen.

In the ammoniacal liquors, cyanogen is found principally under two forms: as ferrocyanide and sulphocyanide of ammonium. Ammonium cyanide exists therein but rarely and in a subsidiary manner.

According to Lewis, ammonium ferrocyanide will be formed by the action of free hydrocyanic acid, in the presence of ammonia.

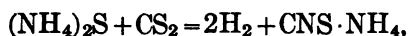
on iron sulphide, which is itself formed by the action of hydrogen sulphide on the iron framework of the condenser:



The ammonium ferrocyanide cannot in any way come from the iron contained in the coal, nor be formed in the retorts because all the ferrocyanides are decomposable at temperatures much lower than those reached in the retorts.

As to the ammonium sulphocyanide, its origin is a little more obscure and still requires some elucidation.

And yet Lewis thinks, from experiments, that it results from the action of carbon bisulphide on ammonium sulphide,



this sulphide of carbon being itself produced by the action of the sulphur of pyrites contained in the coal on the carbon at the temperature of the distillation.

The amount of ferrocyanide and of sulphocyanide of ammonium found in ammoniacal liquors is relatively very small. Lewis estimates that on an average 181 grams of ferrocyanide of ammonium, calculated as Prussian blue, is found in one ton of coal, and of sulphocyanide of ammonium he found 226 to 907 grams per ton of distilled coal.

As the result of experiments carried on in certain German works—at Wiesbaden, Karlsruhe, Mainz—Esop gives the following figures (Chemische Industrie, 1892, page 116).

	Per Cent.	Ammonia in the Ammoniacal Liquors.
Sulphocyanic acid.....	1.22	18.05%
“ “ .....	1.51	19.03%
“ “ .....	2.33	36.05%

Lunge claims that the quantity of sulphocyanide of ammonium contained in the ammoniacal liquors in the manufacture of gas in England amounts to 11 kilos per 454 liters; but Clayfield after numerous experiments was able to find but 0.453 kilo per 454 liters.



It is not at all surprising that the ferrocyanide and the sulphocyanide of ammonium, both very soluble in water, should exist in such small quantities in the ammoniacal liquors; this is due simply to the action of carbonic acid which displaces the hydrocyanic and the sulphocyanic acids from their combinations.

On the other hand, in the purifying materials the cyanogen is retained almost wholly, and if we consult the following table by Lewis, it will easily be seen that immediately after passing through the first purifier the quantity of cyanogen compounds contained in the gas diminishes considerably, and that it is in this first purifier that the greater portion of the cyanogen products formed during the manufacture are collected.

	Hydrocyanic Acid per Cubic Meter.		
After the retorts. ....	19.2	to 30.6	grams.
“ “ condensers. ....	18.9	to 29.0	“
“ “ scrubbers. ....	18.4	to 18.8	“
“ “ 1st purifier. ....	1.2	to 14.2	“
“ “ 2d “ ....	0.5	to 1.2	“
“ “ 3d “ ....	0.45	to 0.50	gram.
“ “ 4th “ ....	0.30	to 0.40	“

Leybold had, moreover, made similar experiments, showing the progressive elimination of cyanogen, with the following results:

	Hydrocyanic Acid per 100 Cu. M.		Hydrocyanic Acid, Per Cent.	
	I.	II.	I.	II.
Conduit. ....	265.9	203.4	5.4	14.57
After condensation. ....	251.6	173.6	45.09	—
“ 1st purifier. ....	131.7	—	—	—
“ 2d “ ....	83.3	59.5	18.2	56.15
“ 3d “ ....	61.6	—	8.16	—
In the gasometer. ....	41.2	19.8	15.5	9.73

The purifying materials are, as is known, composed of a mixture of ferric hydrate and sulphate of lime, obtained by the reaction of time on sulphate of iron; this mixture is then made porous with sawdust.

The gas, on coming into the purifying boxes, contains the following impurities: Hydrogen sulphide, ammonia and cyanogen com-

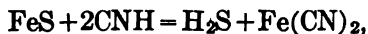
pounds. Rather complex reactions take place in the purifiers between the purifying materials and the impurities, there being formed notably ferrous cyanide, ferrocyanide of iron and ammonium, carbonyl ferrocyanide of sodium, and ammonium sulphocyanide.

The formation of ferrocyanide may be explained in various ways.

The hydrocyanic acid would react on oxid of iron in order to form ferrous cyanide, which in the presence of oxygen of the air would become converted into Prussian blue:



It follows, however, from Leybold's experiments that if a current of hydrocyanic acid mixed with hydrogen be passed through the purifying materials no absorption takes place, while, on the other hand, if the purifying materials be first saturated with hydrogen sulphide the hydrocyanic acid becomes entirely combined, due to the previous formation of iron sulphide, according to the reaction

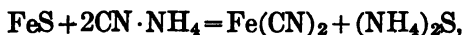


the ferrous cyanide formed then becoming converted into Prussian blue under the action of atmospheric oxygen.

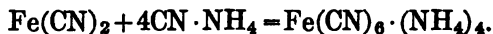
Other investigators claim that the ferrous cyanide results from the action of ammonium cyanide on oxid or sulphide of iron.



or



and if ammonium cyanide be in excess there is formation of ammonium ferrocyanide:



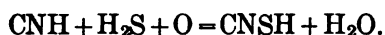
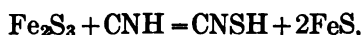
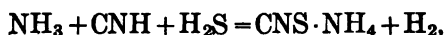
In every case it is to be noted that Prussian blue is not formed directly in the purifiers, but by oxidation of the ferrocyanide. Moisture or the use of steam facilitates the formation of ferrocyanides, whereas ammonia prevents it. It is therefore of the utmost

importance, if one wishes to obtain materials rich in ferrocyanide, to wash the gas as completely as possible, in order to remove the ammonia. By removing the ammonia almost entirely, Knublauch succeeded in obtaining materials containing up to 24% of ferrocyanide of potassium (reckoned on the dry matter).

In fact ammonia, oddly enough, facilitates the formation of sulphocyanide of ammonium or of sulphocyanide of iron. Knublauch in 1877 was the first to show the close relation which exists between ammonia and sulphocyanogen, and he showed how the sulphocyanides may be formed at the expense of ferrocyanides if the washing of the gas has been insufficient.

Sulphocyanide of ammonium exists in but very small quantities in gas as it comes to the purifying boxes, but it may be formed in large amounts in these boxes, especially if ammonia or ammonium sulphide are found in the presence of finely divided sulphur such as exists in the spent oxids or in the presence of hydrogen sulphide.

According to Lewis the reactions which take place on the formation of sulphocyanide are as follows:



Leybold studied this phenomenon and analyzed two purifying masses saturated with hydrogen sulphide which had been subjected to the action of a mixture (1) of hydrocyanic acid and ammonia and (2) hydrocyanic acid and ammonium sulphide:

	I. CNH + NH <sub>3</sub>	II. CNH + (NH <sub>4</sub> ) <sub>2</sub> S.
Water. . . . .	23.60%	33.02%
Sulphur. . . . .	24.98%	11.39%
Prussian blue. . . . .	1.70%	5.38%
Ammonium sulphocyanide. . . . .	3.03%	4.40%
Ammonia. . . . .	2.05%	0.75%

It results from these analyses that, in the case of ammonia, the amount of sulphocyanide formed is, as is known, greater than that of Prussian blue, and that in the case of ammonium sulphide it is about equal.

The presence of an alkali in the purifying materials is likewise very favorable to the formation of the sulphocyanides.

During the "revivification" of these materials, if care be not taken to avoid heating, the formation of sulphocyanides at the expense of ferrocyanides is considerable. Burschell estimates that it may sometimes amount to 30% of the weight of ferrocyanides. This transformation is due to the action of ammonia and of hydrogen sulphide found in the purifying materials, and to the moisture contained therein, and likewise to the action of sulphur and the alkali sulphides on the ferrocyanides.

As may be seen from this rapid review of the complicated reactions which control the formation of cyanogen compounds in the gas itself, in the ammoniacal liquors and in the purifying materials, this formation is intimately dependent upon numerous conditions. The gas-worker who is desirous of recovering the cyanogen should strive to avoid or to produce them according as they are injurious or favorable.

We shall now take up the various processes which the manufacturer may put into operation in order to extract the cyanide compounds.

- A. In the illuminating-gas.
- B. In the ammoniacal liquors.
- C. In the spent oxid.

#### A. DIRECT EXTRACTION FROM GAS.

Although the presence of cyanogen compounds in gas has been known for a long time (it is mentioned in an English patent in 1850), it is only within the last few years, on account of its limited use in the arts, that any attempt has been made to derive any benefit from it. The spent purifying materials, or Laming's mixture, were considered as valueless waste products, and it was not till 1880 that a French manufacturer, Gauthier-Bouchard, thought of utilizing them for the manufacture of Prussian blue and of potassium ferrocyanide. As these cyanogen compounds are formed naturally in these materials, and without care or thought on the part of the manufacturer, this process has been but little improved. But from the time that cyanides became useful in the treatment of aurifer-

ous minerals, many investigators, especially in Germany, perceived the possibility of making gas a profitable source of cyanide production, and sought to extract from gas the greatest amount of cyanide possible. They soon recognized that Laming's mixture, or other similar materials, were but an imperfect and expensive source of production. In fact it is easily understood that this treatment in the dry way has the disadvantage, notwithstanding the porosity which sawdust gives to the mixture, of presenting but a small contact action to the cyanogen and its compounds, and that the absorption of these bodies is necessarily incomplete. Moreover it has already been noticed that on account of secondary reactions appreciable amounts of sulphocyanides may be formed in the materials, which are of less value than are the ferrocyanides, and their subsequent conversion into cyanides is more difficult.

These are the reasons which caused the investigators to seek the extraction of the cyanogen compounds as completely as possible directly from gas. At present these processes seem to prevail among gas manufacturers who are anxious to derive some benefit from such an important by-product, while in the works which, for some groundless reason, persist in refusing to consider the importance of cyanides in gas, the purifying materials are still being worked for the Prussian blue, in order to make of it a better commercial product.

In other works, and they are numerous enough, they do not even try to obtain materials rich in ferrocyanides; and when these materials are spent, i.e. do not absorb any more hydrogen sulphide, they are sold to manufacturers of Prussian blue or of cyanides.

In Germany and England processes for direct extraction of cyanides from gas are established on a large scale, and it is to be hoped that the French will not long remain behind their neighbors.

The ideal method of direct extraction of cyanide compounds from illuminating-gas as it comes from the retorts would be to pass it through an alkaline solution, thus forming an alkali cyanide. But this is quite impossible on account of the presence in gas of other acid gases, e.g. carbonic acid and sulphuric acid which could immediately displace hydrocyanic acid and therefore prevent all formation of cyanide. Therefore the idea of obtaining cyanides directly from gas must be abandoned.

Combinations upon which carbonic acid and hydrogen sulphide have no action must be sought.

**Knublauch's Process.**—Knublauch was the first investigator to become interested in this important question. Knublauch, who since 1877 had undertaken a whole series of researches on cyanogen in illuminating-gas was led during his experiments to find a method which allowed direct extraction of the cyanogen products from gas in a wet way (German patent No. 41930, Aug. 18, 1886 ; French patent No. 209770, Nov. 25, 1890).

This process consists in passing the gas into purifiers, washers, or scrubbers containing in solution one or more of the substances mentioned in the two following groups: (1) alkalis, ammonia, ammoniacal liquors, alkaline earths, magnesia, carbonates and sulphites of these bases; (2) iron, manganese, zinc, oxids, hydrates, or carbonates (natural or artificial) of these metals.

Knublauch noticed that carbonic acid and sulphhydric acid did not in any way interfere, and that even when these two gases were found in large quantity in the gaseous mixture, at the moment of passing through a solution containing both iron and an alkali, cyanogen forms with them ferrocyanide with so great an energy that the affinity of carbonic acid and hydrogen sulphide toward cyanogen is so weakened as to render the amount of hydrogen sulphide absorbed insignificant.

The gas should always pass through a liquid and not a solid mass, and this liquid should be agitated during the passage of the gas, which passes through successively a series of absorption apparatus so arranged as to permit easy change of the order of succession.

If, for example, a gas, such as illuminating-gas, containing, besides cyanogen, carbonic acid and hydrogen sulphide be passed into a solution containing a ferrous salt and an alkali, the precipitated ferrous hydrate,  $\text{Fe}(\text{OH})_2$  disappears almost wholly in the state of soluble alkali ferrocyanide, while only a small portion remains in suspension in the liquid in the form of sulphide of iron. If an amount of iron greater than that of alkali be used, an insoluble cyanide is formed.

The amount of absorbent material to be used for a definite weight of cyanogen depends on the nature of these materials, and the proportions naturally vary as one uses mono or bivalent bases,

hydrates or carbonates, natural or artificial products. In general, for every molecule of hydrocyanic acid, a molecule of alkali, of alkaline earth, hydrate or carbonate, and somewhat less than a molecule of iron compounds should be used. The quantity of liquid used should at least be sufficient to allow the gas to bubble through.

Knublauch's method has received but few trials in England. Its want of success was due not to the results which it yielded but to the lack of interest shown by the manufacturers, at the time of its appearance, for the direct recovery of cyanogen.

**Gasch's Process.**—The process of Robert Gasch of Mainz (patent No. 201377, Dec. 24, 1889) consists in using recently precipitated metallic sulphides, which with the cyanogen of the gas form a ferrocyanide. The indispensable condition is the presence of ammonia, which condition is found in illuminating-gas. The higher the temperature the more rapid and complete is the conversion. It is instantaneous at from 50 to 60°. The action of the heat may be suppressed when the reaction is well begun, and this can be done by adding a cyanide precipitate obtained from a cyanide solution coming from a previous operation. The operation is carried on by means of ordinary washers, or by the means of vertical boilers, which allow intimate contact of the gas with the absorbent materials, and this apparatus is so placed that the gas which passes through it has a temperature not exceeding 36°, a temperature at which sulphocyanides begin to be formed.

According to the author of this process, its advantages are as follows:

- (1) An increased yield in ammonium ferrocyanide.
- (2) High concentration and purity of the cyanide liquors under a form suitable for further treatment.
- (3) The only impurities are a small amount of ammonium and potassium sulphides.

Gasch recommends, moreover, the use of liquids holding in suspension a metallic sulphide such as iron sulphide, to which is added a milk of lime, and having in solution a soluble salt (oxalate or sulphate of alkali, an ammonia salt, sulphate of magnesia, aluminum, iron, etc.).

If, for example, a solution of sodium sulphate be used to which

is added a milk of lime and having in suspension sulphide of iron, a weak solution of sodium ferrocyanide will be obtained containing more or less sodium sulphide and a deposit of sulphate of lime and sulphide of calcium, both insoluble.

**Rowland's Process.**—This process (French patent No. 218215, March 21, 1892) consists essentially in having the ammoniacal liquors of the scrubber absorb the whole or greater part of the cyanogen. For this purpose Rowland adds an iron salt to the water of the scrubber in suitable quantity, but not in such quantity that iron sulphide will be formed. The optimum amount is 5.5%. Ammonium ferrocyanide is formed which remains in solution. After the addition of a fresh quantity of salt or oxid of iron, the ammoniacal liquors are distilled, the addition of iron converting the ammonium ferrocyanide into double ferrocyanide of iron and ammonium, which is insoluble and may be separated from the liquor by adding milk of lime and filtering. The filtered solution is heated to boiling and sulphate or chloride of potassium is added, thus forming a double ferrocyanide of potassium and lime. The same result may be obtained by acidifying the liquor and boiling. The double ferrocyanide of potassium and lime is treated with potassium carbonate, which on ignition converts it into alkali ferrocyanide and carbonate of lime. A strong solution is made and allowed to crystallize.

**Fowlis' Process.**—Fowlis of Glasgow has patented a process (English patent No. 9474, May 18, 1892) which is similar. The gas, previously freed of ammonia, is passed through a solution of potassium or sodium carbonate containing oxid of iron ( $\text{Fe}_2\text{O}_3$ ) or carbonate of iron in suspension. This solution is prepared as follows: To 25 liters of a solution of ferrous chloride ( $\text{FeCl}_2$ ), containing 150 grams Fe per liter, is added a solution of 7.5 kg. carbonate of sodium at  $98^\circ$  in 150 liters water. Carbonate of iron is precipitated, the solution of sodium chloride is decanted, and the carbonate of iron is put in suspension in a solution of 13.5 kg. of carbonate of sodium in 200 liters of water. The 13.5 kg. of carbonate of sodium may be replaced by 17.5 kg. carbonate of potassium. A scrubber provided with several horizontal plates is best suited for this operation. These plates are perforated with numerous small holes, upon which rest tubes covered with a cap forming a hydraulic closing,



as in the distillation columns. The absorbent mixture, contained in a cylinder which is provided with stirrers, flows regularly or in an intermittent manner into the scrubber. It comes to the tubes, falls from one compartment to another, and finally flows through the lower part of the apparatus. In circulating in this way it meets the gas, which flows in the opposite direction, the cyanogen of the gas being thus removed.

The ferrocyanide solution is evaporated to dryness, the tar and other impurities accompanying it being easily removed by redissolving. The clear solution is concentrated and allowed to crystallize.

Speaking concerning Fowlis' process before the English Gas Congress in 1896, Charles Hunt stated that he produces a solution of sodium ferrocyanide which on concentration and crystallization gives 75% sodium ferrocyanide. One must acknowledge that that is already a splendid result setting well in relief the profit which may be gained by the direct extraction of cyanogen from gas.

**Claus and Domeier's Process.**—This process (1895-96) is but a modification of Fowlis' method. These investigators first prepare an absorbent material by fusing a mixture of iron or oxid of iron, sulphate of sodium or potassium, and charcoal. The product of fusion, taken up with water, yields a grayish-black substance, slightly soluble, being a compound of iron and the alkali metal  $\text{Fe}_2\text{Na}_2\text{S}_3$ . This substance is suspended in water and placed in a series of washers, into which the gas, previously freed of ammonia, passes. Ferrocyanide and sulphocyanide of sodium are formed. This process does not form much of the latter salt.

**Schroeder's Process.**—Schroeder proposes to collect all the cyanogen compounds into the ammoniacal liquors (French patent No. 281456). To the waters which are used in absorbing the ammonia, ferrous chloride is added. When the gas passes through this solution, the ammonia of the gas forms a precipitate of iron hydrate,  $\text{Fe}(\text{OH})_2$ , and ammonium chloride; then the hydrogen sulphide converts the hydrated oxid of iron into sulphide of iron, which remains suspended in the absorption waters with oxid of iron; these are dissolved by the ammonium cyanide of the gas, which converts them into ammonium ferrocyanide.

The liquid is distilled in the presence of milk of lime, the ammonia

being thus recovered. Calcium ferrocyanide, slightly soluble, is in part precipitated. To obtain the calcium ferrocyanide still in solution a current of gas freed of ammonia and cyanogen is conducted through the solution, the carbonic acid precipitating the lime. The small amount of calcium ferrocyanide still remaining in solution may be precipitated as Prussian blue by means of a solution of iron perchloride. The precipitate, consisting of calcium ferrocyanide, Prussian blue, and carbonate of lime, is then heated to boiling and treated, with constant stirring, with potassa or potassium carbonate so as to convert the calcium ferrocyanide and the Prussian blue into potassium ferrocyanide, which, being soluble, may be separated from the insoluble carbonate of lime by filtration. The filtered solution is then concentrated and allowed to crystallize.

**Teichmann's Process.**—This process is also based on analogous reactions (French patent No. 290265, June 28, 1890), but instead of using the chloride, this investigator uses the sulphate of iron, and in case of need he employs zinc solutions. In using iron sulphate in the washers, this salt becomes at once converted, by means of hydrogen sulphide and ammonia, into iron sulphide and ammonium sulphide. Then the cyanide of ammonium acts on the iron sulphide, yielding ammonium ferrocyanide.

The greater portion of the cyanogen thus goes into solution, while a small part of it remains insoluble in the form of cyanide of iron. Sulphide of iron dissolves just as fast as ammonium cyanide is absorbed, and by repeated additions of a solution of iron sulphate, solutions containing a high percentage of ammonium ferrocyanide may be obtained.

The absorption apparatus may be inserted between the tar extractor and the apparatus used in absorbing the ammonia. Without fear of obstruction, the ordinary scrubbers or the standard washers may be used. But, when working on a large scale, it is best to place the iron solutions in the washers.

The solutions of ammonium ferrocyanide obtained may be precipitated by means of calcium chloride.

The reaction is the same when zinc salts are used. The precipitated zinc sulphide is converted by the ammonium cyanide into the double cyanide of ammonium and zinc and ammonium sulphide.

By the addition of other zinc salts to the solution of the double cyanide, zinc cyanide may be precipitated which may be converted directly into potassium cyanide.

**Lewis' Process.**—The last process to be mentioned in this class is that by Lewis (*Moniteur Industriel*, 1897, Nos. 26 and 27). This is based likewise on the affinity which cyanogen or hydrocyanic acid has for sulphide of iron held in suspension in an alkaline solution, the object of the process being to obtain a ferrocyanide.

Lewis recommends that the process be carried on as follows:

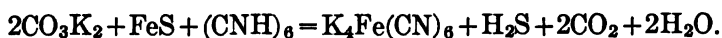
The sulphide of iron is produced by precipitating an iron salt by means of a liquid prepared with the waste gases in the treatment of ammonia.

The sulphide of iron is held in suspension in a specially constructed washer, containing an alkaline solution in which is an excess of soluble iron.

The washer should be so constructed as to allow intimate contact of gas with the suspended iron, and to avoid the formation of a modified ferrocyanide,  $K_7Fe(CN)_{12}$ , which is less stable.

The ammonia should be removed as thoroughly as possible from the gas before the latter be allowed to enter the washer, since the acids of the fixed ammoniacal salts, e.g., ammonium chloride, forms, with the alkali, an alkaline chloride which contaminates the product obtained.

By working carefully and with an efficient system of washers the reaction should theoretically be as follows:



But in reality, as Lewis has stated, there are formed complicated and involved inter-reactions.

That is the chief defect of all the processes which have been reviewed. Their perfect operation depends on numerous conditions chemical as well as mechanical or physical, which influence the results to a very large extent, and unless great care and many precautions be taken in operating these processes, they will be far from being successful. Moreover, these processes all have the disadvantage of producing but very dilute solutions most of the time, and the cost of treating such large quantities of liquids is heavy. These

are the reasons why these methods have received but limited trials, and have never been applied on a large scale.

**Bueb's Process.**—The process invented by J. Bueb, several years ago, is entirely different. This process, now in operation by the Deutsche Continental Gas Gesellschaft of Dessau, has thus far produced very favorable results. This method will be studied somewhat more at length, because it is at present in operation, and because of all the methods for the direct extraction of cyanogen from gas this is almost the only one which deserves to be kept in mind.

In fact, the reactions utilized by Bueb are those mentioned in the processes of Knublauch and others, but with this difference, that instead of seeking to produce a soluble ferrocyanide Bueb produces an insoluble compound.

The principle of this process consists in bringing the gas, previously freed of tar, into intimate contact with a saturated solution of sulphate of iron. The ammonia of the gas, playing the rôle of the alkalis, used in the other processes, a compound of iron, cyanogen, and ammonium is formed, which separates in the form of a light mud.

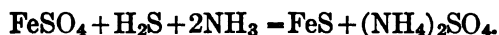
In practice, the operation takes place in an apparatus specially constructed by Bueb on the same principles as the standard washers, with this difference, that instead of flowing automatically into the apparatus the washing liquid passes, at definite intervals, from one chamber to another by means of a pump near the washer. The sulphate of iron solution, previously prepared in a special mixer, is pumped into the last of the four chambers, then from this one to the one preceding, and so on to the first chamber. The cyanogen muds, obtained in the first compartment of the washer, are collected into a forged iron reservoir or into a special vat, to be transferred to suitable vessels if they are to be sold as such, or to be later treated in the works itself, according to processes which will be mentioned further on. The first three compartments are provided with revolving discs similar to those of the standard washers, while the fourth has a stirrer, the object of which is to avoid the thickening which takes place in this chamber.

As these cyanogen muds obtained by this process contain appreciable amounts of ammonia they may be treated for the extrac-

tion of this product, especially if the works have a plant for their treatment. To this end the muds are heated to boiling by means of direct steam in boilers provided with stirrers. The gas thus liberated passes into a cooler where the ammonia condenses whereas the sulphide vapors are conducted into a purifier. The residue is subjected to the action of a filter-press in order to separate the solution of ammonium sulphate from the insoluble cyanogen product. The ammonium sulphate solution which flows from the filter is concentrated and allowed to crystallize. The insoluble residue, which is a blue mass containing about 30% Prussian blue (44% ferrocyanide of potassium), and 4% ammonia, is put in tuns or sacks and sold as such.

In communications made to two successive annual Congresses of the German Gas Industries (Kassel, 1899; Mainz, 1900) Bueb gives the following details concerning the working of his process:

The concentrated solution of iron sulphate introduced into the last compartment should show about 20° B. (That is, should contain 28%  $\text{FeSO}_4 + 7\text{H}_2\text{O}$ .) In this compartment, which is that of the gas outlet, the gas contains only traces of cyanogen, but contains ammonia and hydrogen sulphide, which, coming in contact with the iron sulphate, converts it completely in 6 to 10 hours into sulphide of iron and ammonium sulphate:



On reaching the other compartments this solution of ammonium sulphate, holding sulphide of iron in suspension, meets the gases which are richer and richer in cyanogen and ammonia, and these two bodies reacting on the sulphide of iron form with it an insoluble double salt  $(\text{NH}_4)_2\text{Fe}(\text{CN})_6$ , while hydrogen sulphide is set free, and is carried out of the washer, or remains in part in the product of the reaction in the form of ammonium sulphide:



This reaction is finished completely in the first compartment of the washer.

The reaction in its various stages may, moreover, be followed by the coloration of the absorbent material. In the last compartment, which contains the iron solution, the liquid is black; it becomes

lighter in the others, and in the first it is greenish yellow. The cyanogen mud which results from this operation contains an amount of cyanogen equal to 18.2% of potassium ferrocyanide ( $\text{Fe}(\text{CN})_6\text{K}_4 + 3\text{H}_2\text{O}$ ) and to 12.2 to 13.5% of Prussian blue, besides 6 to 7% of ammonia, an amount which represents about one third of the ammonia obtained in gas-works.

If some double salt still remains in solution it may be made insoluble by simply boiling and without the addition of any reagent. The yield by this process is 95% of the cyanogen, but the results depend much on the kind of coal used.

The English coals are those which contain the most cyanogen. They yield 7.4 grams of potassium ferrocyanide ( $\text{Fe}(\text{CN})_6\text{K}_4 + 3\text{H}_2\text{O}$ ) per cubic meter of gas. In a plant where a mixture of English and Upper Silesian coal is used 5.3 grams are extracted per cubic meter of gas. In another works using a mixture of English and Westphalian coal the yield was 5.6 grams. The coals of the Saar give a yield of 4 to 4.5 grams; those of the north of France 4 to 5 grams; those of the east 4 grams; in general the minimum is 3.5 grams and the maximum is 8 grams.

Furthermore, Bueb's process allows a very simple removal of hydrogen sulphide. Cyanogen possessing the property of decomposing the sulphide of iron recently formed by setting hydrogen sulphide free, it is evident, as Bueb points out, that this property would thwart the absorption of hydrogen sulphide by the purifying materials, which, according to the old processes, should play the double rôle of absorbing cyanogen and hydrogen sulphide. Therefore, purifying materials are obtained containing 50-60% of sulphur.

Bueb has, moreover, observed that his process gives a larger yield the warmer his gas is, that is, that the gas is cooled less before it passes through the absorption apparatus. For this purpose instead of placing the coolers, as is usual, before the cyanogen separators, Bueb places them next to these, i.e., between them and the scrubbers. In this way a smaller amount of ammonia remains in the cyanogen absorption apparatus, and because of this the yield in cyanogen compounds is again increased. Another advantage of this new arrangement is that at the high temperature at which the gas is kept the last traces of tar and naphthalene are easily

removed, and to this end Bueb places another vessel filled with oil before the cyanogen absorption apparatus and connected with it. This oil, being heated by the passing gases, absorbs more easily, at this temperature, a larger amount of tar and naphthalene.

Bueb's process marks a real progress in the extraction of cyanogen from gas, even considering only the results obtained: Thus in the dry way only 50-60% of the cyanogen present in gas could be extracted in well-conducted operations, while by this new process the yield is quantitative. Moreover, the cyanogen may be recovered in a very practical shape, since these products are obtained in such concentrated form as to warrant the expense of transportation, provided the gas-maker does not care to convert them into cyanide.

A. Smits of Amsterdam, without knowing beforehand the investigations of Bueb, in an interesting communication to the International Congress of Gas Industries in 1900, confirms the results obtained by the latter at Dessau by his own experiments made at the gas-works at Amsterdam according to a process similar to that of Bueb.

Smits mentions here the reasons which led him to absorb hydrocyanic acid in the presence of ammonia (*loc. cit*) instead of bringing the gas previously freed of ammonia in contact with a solution of potassium carbonate holding a ferrous salt in suspension:

"It is remarkable that generally the absence of ammonia has been considered as a condition indispensable for a good absorption of hydrocyanic acid. I suppose that we have been led into error by the following phenomenon: When illuminating-gas, coming in contact with the absorbent liquid, contains ammonia analysis shows a less amount of yellow prussiate of potash in the clarified solution, but after having again analyzed the black precipitate, which is always formed during absorption, it is easily proven that this precipitate contains a quantity of cyanogen which is proportional to the amount of ammonia which the gas contained, whence it follows that the total amount of hydrocyanic acid absorbed is in this case greater.

"Now then, in this way an amount of hydrocyanic acid is obtained, which would be lost during absorption in the ammonia apparatus.

"Again, the presence of ammonia helps the formation of an insoluble cyanide, and that is the reason why a smaller amount of

yellow prussiate of potash is formed in the liquid in the presence of ammonia."

"Those are the reasons which led me to suppose that the place where hydrocyanic acid was being absorbed was badly chosen."

Starting with these facts, Smits sought to absorb the hydrocyanic acid by means of a ferrous sulphate solution at the exit of an apparatus where the gas still contains large quantities of ammonia, and like Bueb, he was able to prove that the yield was quantitative.

Thus, as may be seen, the problem of the direct extraction of cyanogen from illuminating-gas is really simple, and at the same time profitable, since it permits the extraction of this cyanogen almost in its entirety.

**Feld's Process.**—Finally shall be mentioned the process for the direct extraction of cyanogen from gas, just recently patented by Feld (French patent No. 317382, Sept. 1901), and which certainly does not lack in originality.

It consists in absorbing the cyanogen in such form that it may then be recovered by simply heating to boiling, in the state of pure hydrocyanic acid, which may then be absorbed by ordinary reagents—whereas the impurities of the gas are either previously removed or are in great part unabsorbed.

Feld divides the substances capable of absorbing cyanogen under these conditions into three groups:

*First group.*—Basic or carbonated compounds, which in aqueous solutions, or in suspension in water or salt solution, absorb hydrocyanic acid, and afterwards give it off on boiling. These are compounds of magnesium, aluminium, zinc, manganese, and lead. They may further be divided into three subgroups:

(a) Those which absorb  $\text{CNH}$  and  $\text{CO}_2$  and leave  $\text{H}_2\text{S}$ . These are basic compounds of magnesium.

(b) Those which absorb  $\text{CNH}$ , but neither  $\text{CO}_2$  nor  $\text{H}_2\text{S}$ . These are the basic compounds of aluminium and magnesium carbonate.

(c) Those which absorb  $\text{CNH}$  and  $\text{H}_2\text{S}$  but not  $\text{CO}_2$ . (Basic compounds of zinc, manganese, and lead.)

*Second group.*—Compounds which in basic, neutral, or acid solution, or in suspension in water or in saline or acid solution, absorb hydrocyanic acid, and give it up completely on boiling only



in the presence of acid. To this group belong the compounds of copper, mercury, and the ferric and ferrous salts. The iron compounds give up the hydrocyanic acid completely only when they are not intermixed.

*Third group.*—Compounds which when hot even in basic solution or in suspension in water, and in the presence of salts of the first group, do not absorb hydrocyanic acid, but decompose hydro-sulphuric acid.

In this group are included ferric and ferrous salts either separate or mixed.

#### B. EXTRACTION OF CYANOGEN COMPOUNDS FROM THE AMMONIACAL LIQUORS OF GAS.

As we have seen at the beginning of this chapter, the ammoniacal liquors contain a certain amount of cyanogen in the form of ferro-cyanide and sulphocyanide of ammonium. The amount of the former varies, on an average, from 150–180 grams, calculated as Prussian blue, per ton of coal. The amount of ammonium sulphocyanide present in ammoniacal liquors is quite variable, and depends much on the length of time they have been stored. Thus, in the same liquors, Lewis found 1.76, 3.5, and 4 grams sulphocyanide at intervals of one month. Generally one ton of spent gas-liquors, that is, having been subjected to distillation of ammonia, yields, on an average, 6 kg., of ammonium sulphocyanide.

Formerly the operation was carried on as follows: After the gas-liquors had been distilled in the presence of lime in order to recover the ammonia, they were allowed to stand, and to the clear solution were added equal amounts of copper sulphate and iron sulphate. Copper sulphocyanide was thus formed, which was decomposed by means of ammonium sulphide with formation of ammonium sulphocyanide (Spence's process).

Later the ammonium sulphide was replaced by barium sulphide.

**Pendrie's Process.**—The object of this invention (French patent No. 189648, March 28, 1888) is to recover the cyanogen compounds of the ammoniacal liquors in the form of Prussian blue.

The residues, after the distillation of the ammonia, are allowed to stand until clarified and then decanted. Ordinary sulphuric acid is then added to acid reaction in order to remove any hydrogen

sulphide contained therein. A portion of the hydrogen sulphide is set free, another portion is decomposed. The whole is allowed to stand 24 hours, during which the sulphur and sulphate of lime settle. The solution is decanted, and to the liquid is added a suitable quantity of a ferric salt, Prussian blue being precipitated. This may be converted into potassium ferrocyanide, after having first decanted the solution, and allowing the Prussian blue to stand in contact several days, with a lye made of caustic potash or potassium carbonate.

**Bower's Process.**—Bower (German patent of Dec. 23, 1895), recommends the precipitation of ferrocyanides and sulphocyanides by means of a copper salt in order to form insoluble ferrocyanide and sulphocyanide of copper. A mixture of these two salts, when treated with iron, yields on the one hand insoluble ferrocyanide of iron, and on the other soluble sulphocyanide, which may therefore be easily separated. In practice Bower recommends carrying on the process as follows:

Before distilling, the ammoniacal liquors are treated with magnetic iron either alone or with the addition of an iron salt, in sufficient quantity to convert all the cyanogen into the form of ferrocyanide and sulphocyanide of iron.

The liquors are then distilled in the presence of quicklime in a boiler provided with a stirrer. The residual liquors, containing ferrocyanide and sulphocyanide of calcium, are then treated with a solution of cuprous chloride in sufficient quantity to precipitate the whole of the cyanogen compounds as insoluble salts.

The precipitate is collected, washed, and, while still moist, treated with finely divided iron. The iron replaces the copper, yielding insoluble ferrocyanide, and soluble sulphocyanide. These are separated by filtration.

The ferrocyanide of iron is then treated at the boiling-point, with an alkali, in order to obtain a soluble alkali ferrocyanide, which is purified by crystallization. The solution of sulphocyanide is concentrated and allowed to crystallize.

**Lewis' Process.**—Somewhat different is the process of Lewis and Cripps (English patent No. 5184, March 7, 1896), the method of procedure of which is as follows: After distilling off the ammonia by the usual method with lime, the residual liquors contain the

ferrocyanide and the sulphocyanide in the form of lime salts  $(\text{CNS})_2\text{Ca}$  and  $\text{Ca}_2\text{Fe}(\text{CN})_6$ . This liquor flows from the stills into a suction reservoir whence a pump drives it to the top of a tower, filled with pieces of coke or brick, through which it filters, encountering on its way down an inverse current of sulphurous acid and carbonic acid, which is obtained by passing the waste gases of an ammonia distillation over a grate which burns the hydrogen sulphide and converts it into sulphurous acid. The action of this gaseous current neutralizes and acidifies the originally alkaline liquid. On emerging from the tower the acid solution flows into a long reservoir divided into two unequal compartments. The solution first comes to the larger compartment where it is treated with a solution containing ferrous and ferric salts in order to precipitate the ferrocyanide as Prussian blue. The liquid passes from one compartment into the other, thus allowing the Prussian blue precipitate time in which to settle. The supernatant liquid then flows into a special reservoir, there to be treated with a view to the recovery of the sulphocyanides.

For this purpose a copper sulphate solution is added to the liquid, there being formed an insoluble white precipitate of cuprous sulphocyanide:



The previous treatment with sulphurous acid is absolutely necessary, otherwise there would be formed a partially soluble black copper sulphocyanide.

The cuprous sulphocyanide precipitate is separated by decantation and washed. It is treated with a solution of alkali sulphhydrate which forms a soluble alkali sulphocyanide and an insoluble copper sulphide. The alkali hydrosulphate is likewise obtained by utilizing the waste gas of an ammonia distillation, these gases passing through a washer filled with a strong caustic alkali solution. When the copper sulphide is exposed to air and then treated with an acid, the copper salt employed in the precipitation is "revivified," and may be used over again.

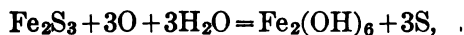
C. THE EXTRACTION OF CYANOGEN COMPOUNDS FROM THE  
PURIFYING MATERIALS OF GAS.

The purifying materials which are used for the chemical purification of gas still constitute, in the works where the direct extraction of the cyanide compounds is not in operation (and they are the larger number), an important source of these products. As has already been seen, these materials contain almost the whole of the cyanogen formed during the manufacture of gas, and it has likewise been shown that the other impurities, especially hydrogen sulphide, are also absorbed therein.

The composition of the purifying materials varies in different works and in different countries. Generally mixtures of lime and ferrous sulphate or oxid of iron are still used. In Germany and in Belgium, purifying materials are used on a large scale, composed entirely of artificial oxids of iron, especially the brown oxid, known under the name of limonite. The hydrated and moist oxid seems to be preferable for the absorption. Below the composition of two limonites is given:

	I. Holland.	II. Belgium.
Sesquioxid of iron. ....	51.30	59.14
Alumina. ....	1.17	0.98
Lime and magnesia. ....	1.63	0.59
Silica. ....	4.97	5.23
Organic substances. ....	26.26	19.64
Water. ....	14.02	15.13
Loss and undetermined. ....	0.63	1.09

These purifying materials are converted, on account of the passage of gas through them, into sulphur, sulphide of iron, ferrous ferrocyanide, sulphocyanide of iron, etc., and the moment necessarily arrives when they become inactive. In order to revivify them they are spread out on a flat surface, where they are constantly stirred with a shovel. The oxygen of the air converts the inactive sulphide of iron into the active oxid and sulphur,



and the ferrous ferrocyanide into Prussian blue. The same mixture may be revivified several times, the result being that an appre-

cialable part of the oxid of iron becomes converted into Prussian blue (which may be recognized by the greenish-blue color which the materials assume) and the sulphur accumulates in such quantities (30 to 40%) that the mixture no longer exerts any purifying action.

It is in this state that it is known as spent oxid, which is immediately treated or more generally sold to manufacturers of Prussian blue or of prussiates.

Its composition varies naturally according to a great many circumstances: kind of coal distilled, method of distillation, the composition of the purifying materials, the degree of fineness of the same, the method of revivification, etc.

According to Esop, the sulphocyanic content varies from 0.39 to 4.25%, the potassium ferrocyanide from 3.02 to 4.58%, the ammonia from 0.49 to 4.38%. Below are given some analyses of purifying materials.

#### ANALYSES OF SOME SPENT OXIDS.

##### LAMING MIXTURE.

Sulphur.....	41.79%
Prussian blue.....	7.37
Sulphocyanic acid.....	3.01
Hydroferrocyanic acid.....	1.01

##### LUX MASS.

Sulphur.....	40.75%
Prussian blue.....	3.08
Ammonium sulphocyanide.....	5.14
Ammonia.....	2.23

##### NATURAL OXID OF IRON.

	I	II
Sulphur.....	30.58%	30.03%
Prussian blue.....	6.30	8.62
Ammonium sulphocyanide.....	4.08	2.12
Ammonia.....	0.41	1.30

Formerly the spent oxids were considered as useless residues, but manufacturers have learned how to derive benefit therefrom,

## ANALYSES OF PURIFYING MATERIALS.

	Leming's Mixture. Bunte's Analyses after 8 Revivifica- tions.	Hydrate of Iron Precipitated.	Limonite.	Sulphate of Iron.	Oxid of Iron, Poor Quality.
Sulphur. ....	33.50	62.44 to 67.18	48.76 to 57.44	48.76 to 55.44	32.42 to 42.16
Hydrate of iron. ....	16.82	17.74 to 19.36	15.96 to 26.42	5.04 to 6.84	8.72 to 20.40
Ammonium ferrocyanide. ....	4.40	trace	trace to 0.21	0.27 to 0.64	trace to 0.44
Prussian blue. ....	11.12	—	trace to 0.17	0.27 to 1.74	trace to 0.64
Ammonium sulphocyanide. ....	14.08	1.99 to 2.74	0.94 to 1.93	1.98 to 3.41	1.18 to 4.72
Ammonium sulphate. ....	0.77	—	—	12.78 to 16.72	— to 1.14
Sulphate of lime. ....	19.31	—	—	trace to 1.74	trace to 3.23
Carbonate of lime. ....		— to 1.04	0.94 to 1.73	—	— to 10.36
Substances insoluble in HCl. ....		3.66 to 5.74	0.71 to 11.42	7.82 to 12.68	12.12 to 20.71
Sawdust. ....		1.98 to 4.72	1.14 to 3.72	1.04 to 3.24	2.16 to 9.76
Tar products. ....		0.72 to 1.22	0.92 to 1.14	0.72 to 1.18	0.55 to 1.04
Water. ....		4.72 to 5.76	7.22 to 10.82	7.98 to 9.22	7.49 to 33.41

and to-day they are treated with a view to the extraction from them of sulphur ammonium sulphate and cyanogen compounds.

**Gauthier-Bouchard's Process.**—To Gauthier-Bouchard is due the idea of utilizing the purifying materials for the manufacture of potassium ferrocyanide. This process, which was set up in a works at Aubervilliers, was operated as follows:

The materials were first subjected to lixiviation with cold water for the purpose of removing all the soluble salts (sulphocyanide of iron and ammonium and the ammonia salts). The insoluble residue was intimately mixed with hydrated lime in the proportion of 30 kg. of lime per cubic meter or 1600 kg. of washed materials. Water was added and the whole stirred. After standing several hours, the mixture was again lixiviated with cold water.

The residues obtained from these washings are exposed to the air for 3 or 4 months and again treated with water. The washwaters contain ferrocyanides in the form of lime salt. The first washings, which are more concentrated, are treated with potassium carbonate, there being formed insoluble carbonate of lime, whereas the potassium ferrocyanide remains in solution. This latter is decanted, concentrated, and crystallized. The final washings, which are too dilute to be thus profitably treated, are treated with a solution of iron protosulphate; a white precipitate of ferrocyanide of iron is formed, which on standing in the air becomes converted into Prussian blue.

In his works at Aubervilliers, Gauthier-Bouchard succeeded, by this process, in extracting 22,500 kg. of Prussian blue from the 1500 cu.m. of spent oxid furnished him by the Parisian gas company, or an average of 15 kg. per cubic meter. The potassium ferrocyanide produced by the Gauthier-Bouchard process brought 275 francs per 100 kg. And yet, while recognizing the advantages of this process, most of the investigators of that time preferred the ignition of the nitrogenous organic substances, notwithstanding the empiricism and the imperfections of this latter process.

At present the Gauthier-Bouchard process, somewhat modified, is in operation in Camille Arnoul's works at St.-Ouen-l'Aumône, where it was installed in 1875.

Moreover, almost all the processes which treat the spent oxids with a view to the recovery of the cyanogen compounds are modi-

fications of the Gauthier-Bouchard process. The improvements made in the process refer especially to the treatment with water and to the conversion into potassium ferrocyanide.

The processes at present in use differ very little. They may be divided into two groups:

The first group includes those processes in which the spent oxid is previously treated with carbon bisulphide in order to remove the sulphur which is present in rather large quantities.

In the second group the cyanogen compounds are immediately extracted. These are the ones which are mostly in use, and they will now be studied. Their operation may be divided into three principal stages:

(1) Lixiviation of the materials in order to remove the soluble salts (ammoniacal salts and sulphocyanides) and to recover the ammonia and the sulphocyanides.

(2) Conversion of the insoluble ferrocyanides into soluble ferrocyanides (sodium and calcium).

(3) Conversion of the calcium or sodium ferrocyanide into that of potassium.

(1) LIXIVIATION.—As has just been remarked the object of this is to remove the soluble salts, which consist especially of ammonium sulphate, sulphocyanides of ammonium and iron, and some iron sulphate. The lixiviation of the materials takes place in filtering-vats arranged generally in series of eight on stands or blocks. These vats may be of iron, though ordinarily they are made of wood, and are 2 meters square and 0.90 meter high, their capacity being about 3000 kg. spent oxid. They are fitted up with a false bottom, consisting of a wooden frame *B* (Fig. 19) resting on wooden beams. This frame is covered with a layer, 10 cm. in depth, of twigs or straw (*A*), and this layer is itself covered with a cotton or jute filtering-cloth *D*. A tap *R* allows the liquid of the false bottom to flow into a wooden or cement trench which communicates by openings, closed with plugs, with three cisterns (*A*, *B*, *C*) (Fig. 20).

The lixiviation is carried on as follows: The purifying materials are first shoveled into the vats and water is then allowed to flow into vat No. 1 so as to cover the materials to the extent of a few millimeters only. This is allowed to stand 12-24 hours, at the end of which time the liquor is drawn off into the trench and



collected in the cistern *A*, and from there it is pumped into vat No. 2, at the same time vat No. 1 is treated with a fresh supply of water. The water is again allowed to stand in contact with the materials for 24 hours, when the liquid is withdrawn from vat No. 2 and collected in cistern *B*, from which it is pumped into vat No. 3. The liquid is also drawn off from vat No. 1 into cistern *A*, from which it is pumped into vat No. 2, and so on. At the end of the treatment the strong liquors show 10-14° B. and contain

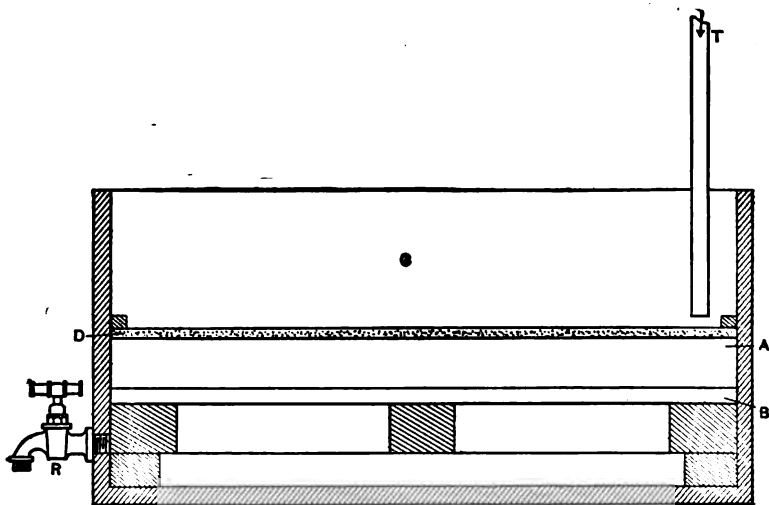


FIG. 19.

about 40 grams of ammonia per liter. The pump transfers the liquid from cistern *C* to an upper reservoir, where it will be taken up again and distilled with lime in order to obtain the ammonia. This is done in the usual way and with the ordinary apparatus used in the recovery of ammonia from the ammoniacal liquors. After the distillation, there remains in solution calcium sulphocyanide, which is later converted into potassium sulphocyanide.

(2) CONVERSION OF THE INSOLUBLE INTO THE SOLUBLE FERRO-CYANIDES.—This may be carried on in two ways:

(a) In an apparatus fitted up with a stirrer, similar to that in Fig. 21.

(b) In filtering-vats similar in every respect to those used in the lixiviation of the materials.

The former apparatus, provided with a stirrer, is generally a

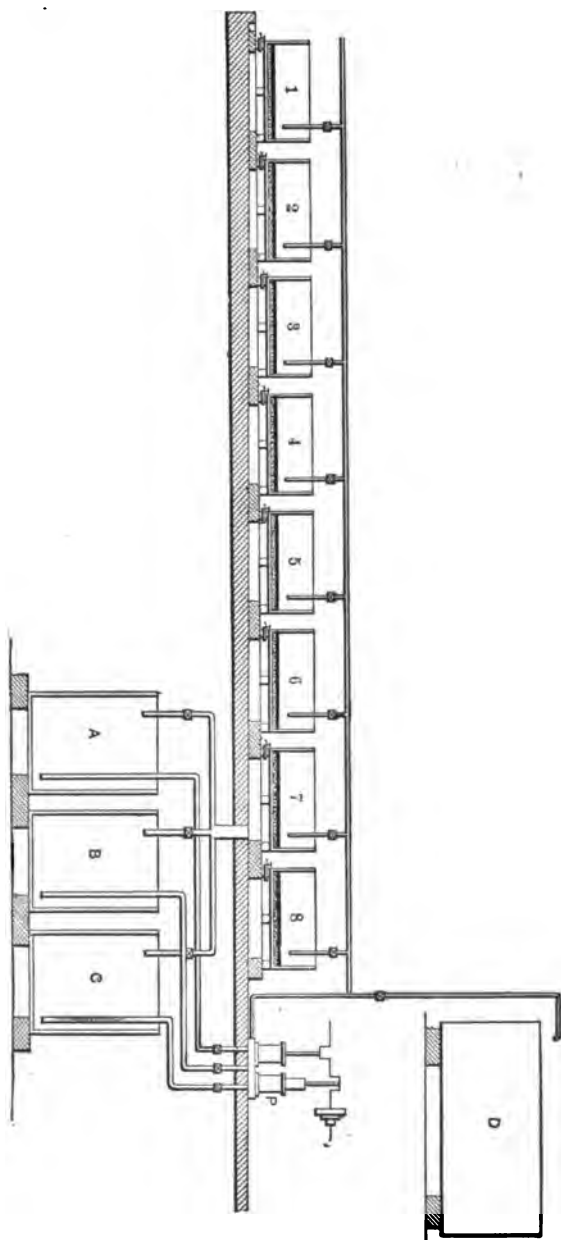


Fig. 20.—Vertical Section of a Battery of Vats for the Lixiviation of Spent Oxid.

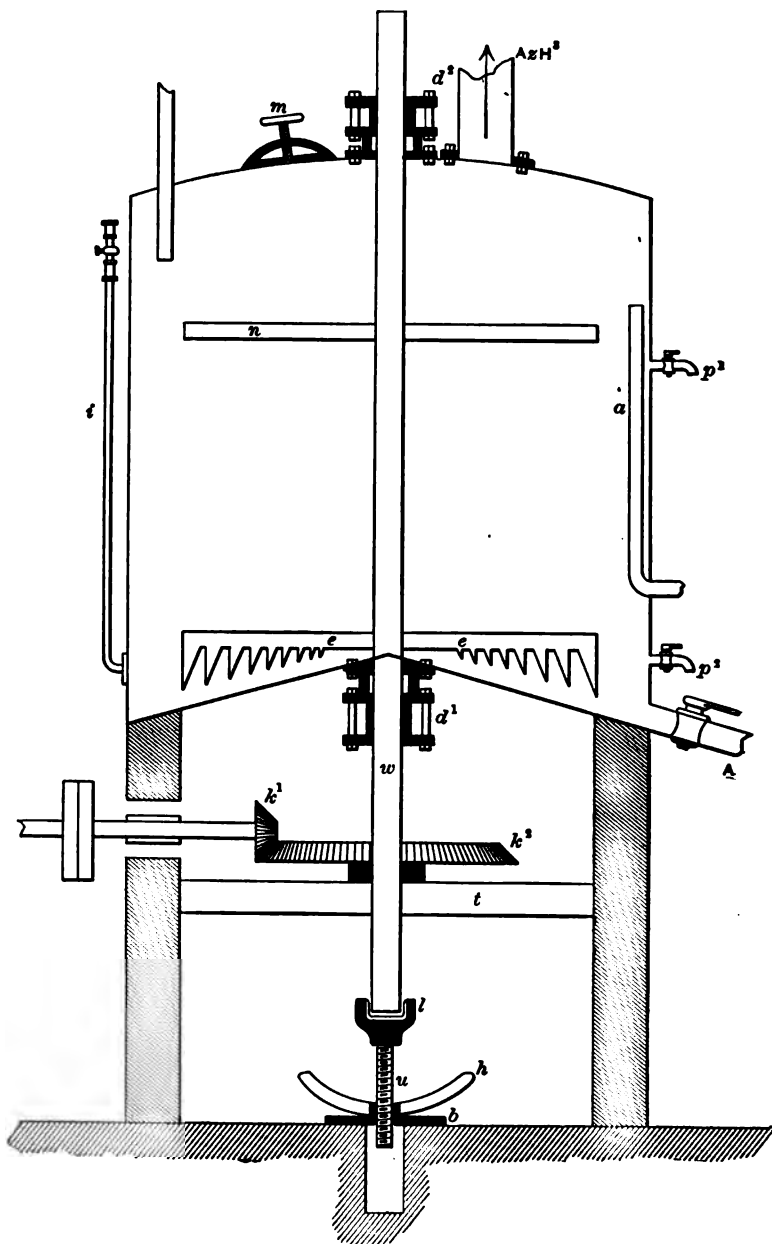


FIG. 21.—Apparatus Fitted with a Stirrer for the Conversion of the Insoluble Cyanides into the Soluble.

kettle or boiler made of 10-mm. cast iron, with a capacity of 6000 liters, and ordinarily receiving 2000–3000 kg. spent oxid. First, the dilute lixivium is conducted into the apparatus and then 2000–3000 kg. of the materials are added. The stirrer is set in motion, the whole being heated with steam. The mud-like mass flows into the filter-presses in order to separate the solution which contains 20–50 grams of ferrocyanide, expressed as potassium ferrocyanide, per liter.

The mass is first pulverized with a specially constructed powder, then sifted through a 4-mm. sieve, mixed with lime and soda in amounts varying with the composition of the mass (which has been previously analyzed) and then treated in the boiler.

When using the filtering-vats the operation is carried on as follows:

After having been subjected to the first lixiviation the materials are allowed to stand several days in order to drain. They are then spread upon asphalt or cement surfaces so as to dry them. The drying may be hastened by frequently turning the mass about with a shovel, this turning also serving to break the lumps. When the mass is dry it is sifted through a 4-mm. sieve, then the sifted mass is mixed intimately with powdered slack lime, in amounts carefully determined by a previous analysis of the mass. Then the filtering-vats, which are arranged as in the first lixiviation, are charged with this mixture, and water is added so as to cover the materials to the extent of a few millimeters. It is allowed to stand 12 to 24 hours, and the operation is carried on as in the first lixiviation. Generally eight or ten vats are used, and lixiviums are obtained showing 12–14° B., containing from 120–140 grams of  $\text{Fe}(\text{CN})_6\text{K}_4 + 3\text{H}_2\text{O}$  per liter, whereas with the stirring apparatus the solutions contained but 40–50 grams of  $\text{Fe}(\text{CN})_6\text{K}_4$ .

(3) PRECIPITATION OF FERROCYANIDES.—The lixiviums obtained by using the stirring apparatus contain ferrocyanide of calcium and sodium, whereas those which are produced by the filtering-vats contain the whole of the ferrocyanide in the form of calcium ferrocyanide,  $\text{Ca}_2\text{Fe}(\text{CN})_6$ . Both of them likewise contain sulphocyanide of calcium and ammonium. The object of the following treatment is to precipitate the ferrocyanides, and this may be done in one of three ways:

- (a) By means of iron salts.
- (b) By means of ammoniacal salts.

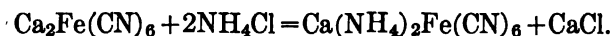
(c) By means of potassium chloride.

*Precipitation by Means of Iron Salts.*—This consists simply in precipitating the ferrocyanides in the form of Prussian blue. If the lixiviums contain the calcium ferrocyanide they are treated with ferrous or ferric chloride; if, on the other hand, they contain sodium ferrocyanide, sulphate of iron is used.

The solution obtained with the stirring apparatus always contains sulphides, and on account of the presence of free ammonia they are alkaline. The solutions are acidified in a special vat and are allowed to stand in order that the sulphur may separate out; after which the clear liquid is decanted and subjected to precipitation with an iron salt.

On account of being cheaper, the use of the ferrous salts ( $\text{FeCl}_2$  or  $\text{FeSO}_4$ ) is preferred, the precipitate being oxidized in air. Precipitation is carried on in wooden or iron vats, the iron solution being gradually added, stirring the while, and from time to time a sample of the liquors is tested to make sure that the precipitation is complete. When this point is reached the whole is allowed to stand at least 24 hours, and then the supernatant liquid is drawn off. The Prussian blue is subjected to the filter-presses and then converted into potassium ferrocyanide by treatment with potash or with potassium carbonate.

*Precipitation by Means of Ammoniacal Salts.*—This process is based on the insolubility of the double salt  $\text{Ca}(\text{NH}_4)_2\text{Fe}(\text{CN})_6$ :

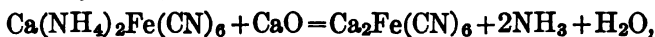


Sal ammoniac as such is never used; but instead the operation is carried on in such a way that the salt is produced in sufficient amount at the time of the precipitation by taking care to obtain lixiviums which contain enough ammonia so that it will be necessary to neutralize them with hydrochloric acid. It is well for this purpose to add to the lixiviated materials a small amount of a mixture of non-lixiviated materials and lime, which will produce the ammonia necessary to the reaction. The operation is carried on in a stirring apparatus which is kept constantly in motion, hydrochloric acid being added until the reaction is acid. The whole is then heated to  $80^\circ$  when the double salt separates out as a white

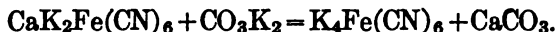
powder with a slight bluish tint. When the precipitation is finished, the stirring is stopped and the precipitate allowed to settle. The clear liquid is drawn off, the precipitate being subjected to the filter-press. As the double salt is not entirely insoluble in water (there remaining 3.75 grams per liter at 25°) it is well to precipitate the mother liquors in the form of Prussian blue by means of an iron salt.

The double salt  $\text{Ca}(\text{NH}_4)_2\text{Fe}(\text{CN})_6$  may be treated:

(1) With lime, in a stirring apparatus, so as to produce pure calcium ferrocyanide,



which may then be converted into potassium ferrocyanide by precipitating a double salt  $\text{CaK}_2\text{Fe}(\text{CN})_6$  by means of potassium chloride, and then converting this double salt into potassium ferrocyanide by boiling with potassium carbonate:

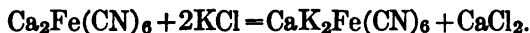


(2) With potassium carbonate in the presence of lime:

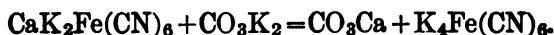


In this way solutions of potassium ferrocyanide are obtained which are concentrated to 30° B. and then allowed to crystallize.

*Precipitation by Means of Potassium Chloride.*—This reaction gives rise to the formation of a slightly soluble double salt,  $\text{CaK}_2\text{Fe}(\text{CN})_6$ :



The precipitation may be done either directly in the calcium ferrocyanide solutions containing at least 100 grams of  $\text{K}_4\text{Fe}(\text{CN})_6$ , or in the same solutions after concentration to 20–25° B. The operation is carried on at 80° in a small kettle or boiler provided with a stirrer. An excess of potassium chloride, added in the form of crystals, should be used. The double salt  $\text{CaK}_2\text{Fe}(\text{CN})_6$  is precipitated as a light-yellow powder, which may be separated by decantation or filtration, and then washed with water, and finally treated with potassium carbonate so as to obtain ferrocyanide of potassium according to the reaction



**RECOVERY OF THE SULPHOCYANIDES.**—These are found in the waters of the first lixiviation in the form of calcium sulphocyanide. They may be extracted by treating the residual solutions from the ammonia distillation by precipitation with a sodium or potassium salt, concentration and crystallization. They may also be precipitated in the form of copper sulphocyanide, which is then decomposed by alkaline sulphide. The same mode of treatment is applicable to other residual solutions containing sulphocyanides.

In other works, sulphur which is always present in these masses in amounts varying generally from 30% to 40%, but sometimes reaching 60% and more, is first of all extracted. Various means may be used in bringing this about: carbon bisulphide, or oil of tar may be used. In other works the sulphur is extracted by fusion with water under high pressure in closed boilers. Finally, a works at Marseilles withdraws the sulphur by means of superheated steam obtaining in this way flowers of sulphur.

But the sulphur which is obtained by these various methods is always more or less dark in color due to the tarry substances, which prevents its use as a commercial and industrial product. All in all, this extraction can but give a small profit, and therefore it is but little used. The works which carry on the extraction of sulphur prefer subjecting the spent oxides to ignition in layer-kilns, according to the Malétra system for the extraction of cyanide compounds. The sulphurous acid thus formed is utilized in the production of sulphuric acid. There is one objection to this, which is that the sulphurous acid is mixed with carbonic acid produced by the carbonization of the tar products, and, on the other hand, a part of the sulphurous acid is continued with the lime which is always in excess in the exhausted and treated materials.

Moreover, various methods have been proposed for the extraction of cyanogen compounds from purifying materials, but very few of them have been tried on an industrial scale; they will, however, be passed in review.

**Valentin's Process.**—Valentin (English patent No. 3908, Nov. 12, 1874) recommended treating the materials with water in order to remove the soluble salts, and then to treat the residues of this washing with carbonate of lime or magnesia, or a mixture of the two, at the boiling-point. There are thus formed ferrocyanides of mag-

nesium and of calcium, which remain in solution, and which may then be precipitated in the form of Prussian blue.

**Harcourt's Process.**—Harcourt (1875) first treats the materials with sulphuric acid, the sulphates of iron and ammonium dissolving, whereas the sulphur and the Prussian blue remain insoluble. The Prussian blue is separated by means of ammonia and reprecipitated from the solution with an iron salt. Harcourt converts the sulphocyanides into ammonium sulphate by means of sulphuric acid and manganese dioxid.

**Kunheim's Process.**—Kunheim and Zimmermann (German patent No. 26884, July 6, 1883) remove the sulphur and the soluble substances from the materials, which are then pulverized, sifted, and mixed with lime, and treated as follows: The mixture is heated in a closed vessel at a temperature between 40° and 100°; the ammonia, united to the ferrocyanogen, distills and is collected. The solution of calcium ferrocyanide obtained is treated in the usual way in order to convert it into Prussian blue, or else evaporated and treated with potassium chloride in order to form a double cyanide  $\text{CaK}_2\text{Fe}(\text{CN})_6$ , which may then be converted into potassium ferrocyanide by means of potassium carbonate. The materials, mixed with lime, may also be treated directly with water, thus obtaining an ammoniacal solution of calcium ferrocyanide, which on careful treatment under definite conditions, in the warmth, yields a precipitate of ferrocyanide of calcium and ammonium difficultly soluble in water. When this precipitate is treated in a closed vessel with lime it yields pure calcium ferrocyanide, while the ammonia distills off. The calcium ferrocyanide is then converted into Prussian blue or into yellow prussiate by the ordinary methods.

**Hempel's Process.**—The process of Hempel and Steinberg (German patent No. 33936, Nov. 21, 1884) consists in first extracting the masses with water at 60° C., and then treating them at the ordinary temperature with a 10% ammonia solution in quantities four or five times more than sufficient to convert them into ammonium ferrocyanide, which latter is then converted into Prussian blue or yellow prussiate.

**Wolfrum's Process.**—In this process (German patent No. 40215, Nov. 14, 1886) the masses are first treated with dilute sulphuric or hydrochloric acid. The acid solution thus obtained is neutralized



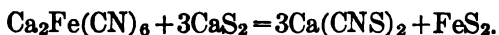
with oxid of iron. The ammonium sulphocyanide is thus decomposed, as is likewise the ammonium ferrocyanide; sulphate of ammonium is formed, whereas Berlin blue, sulphur, and hydroferrocyanic acid are precipitated. Sulphur is extracted by means of carbon bisulphide in suitable apparatus.

**Donath's Process.**—Donath and Ornstein's process (German patent No. 110097, May 29, 1898) is based on the characteristic which Berlin blue possesses of dissolving in concentrated hydrochloric acid, and being reprecipitated when the solution is evaporated or when it is allowed to stand in air. The materials are first treated with very dilute acid so as to dissolve the oxid of iron. The residue is dried, and treated with concentrated hydrochloric acid, the Berlin blue dissolving and imparting to the solution a light-yellow color. It is precipitated from this solution by the addition of water, the precipitate appearing in the form of small crystalline needles.

**Richter's Process.**—Richter (French patent No. 196144, 1889) begins by heating the materials in closed vessels by means of a stream of water-vapor. The ammonia which is set free is collected in sulphuric acid. The residue is likewise treated in a closed vessel with hydrochloric acid so as to obtain iron perchloride. The residue from this treatment is then mixed with magnesium carbonate and treated with water in order to extract the magnesium ferrocyanide which may be converted by the ordinary methods.

**Esop's Process.**—Esop recommends (*Ztsch. für angewandte Chemie* 1889) digesting the masses with water and then subjecting them to the filter-press, the residue being treated with lime and sodium sulphate, a mixture which it seems gives better results than lime alone.

**Marasse's Process.**—Marasse of Berlin converts the whole of the ferrocyanide of the purifying materials into sulphocyanides (French patent No. 158731, Nov. 22, 1883). After having treated the materials with water they are heated in a closed vessel at a temperature above 100° C. and in the presence of an excess of lime, the amount of lime being determined according to the quantity of ferrocyanides in the materials to be treated. At first there is formed calcium ferrocyanide and calcium sulphide, which latter acts upon the ferrocyanide forming calcium sulphocyanide:



According to Marasse the decomposition is complete(?). The solution of calcium sulphocyanide is purified and converted into ferrocyanide by means of finely divided iron. The lime may be replaced by potassa or soda.

**Holbling's Process.**—Holbling (*Ztsch. für angew. Chemie* 1897) proposes a similar method, which consists in the conversion of the Prussian blue contained in the purifying materials into barium sulphocyanide by simply heating the materials during several hours in the presence of a slight excess of barium sulphide (5%), or only one-half hour with a large excess (10 to 15%), and under a pressure of three atmospheres. Holbling claims that the conversion is complete. It is filtered and the solution of barium sulphocyanide obtained is treated by a current of sulphurous acid, or better carbonic acid, in order to decompose the excess of barium sulphide and to convert it into barium thiosulphate and sulphur, or into barium carbonate respectively, which being insoluble are separated by filtration.

**Lewis' Process.**—The following process is recommended by Lewis: After having removed the sulphur from the purifying materials they are boiled with milk of lime. The solution thus obtained, containing ferrocyanide and sulphocyanide of calcium, is treated with sulphurous acid, and a solution of ferrous-ferric sulphate which causes the formation of Prussian blue. This is filtered, and from the residual solution the sulphocyanides are removed by means of a copper salt, as in the treatment of the ammoniacal liquors.

**Maschow's Process.**—The last process concerning the treatment of purifying materials in order to remove from them the cyanogen compounds to be mentioned is that very original one of Maschow (French patent No. 301916, 1901). Maschow makes use of the characteristic which ammonia possesses of dissolving the alkali cyanides. Toward this end he converts the cyanogen compounds into alkali cyanides soluble in ammonia, whereas the other impurities are converted into products insoluble in that reagent. The materials are dried and then mixed with any one of the following substances: Sodium, magnesium, aluminium, iron, zinc, or their oxides, or carbonates mixed with charcoal, or with calcium carbide, or even with both these substances. Either one or the other of these substances is

used, depending upon the composition of the materials. Thus, if the materials are rich in sulphocyanides, metallic iron should be added to the charcoal or to the potassium carbonate used. The mixture is then heated out of contact of air, or in the presence of an inert gas, at such a temperature that the whole of the cyanogen is converted into alkali cyanide, which may then be dissolved in ammonia, the impurities remaining insoluble.

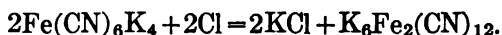
## CHAPTER VIII.

### MANUFACTURE OF FERRICYANIDES.

POTASSIUM ferricyanide ( $K_3Fe_2(CN)_{12}$ ), or red prussiate of potash as it is more generally known in the arts and in commerce, is of sufficient importance industrially to require some mention relating to its preparation.

It is always obtained by the oxidation of potassium ferrocyanide.

**The Chlorine Process.**—The oldest process, and one still in use, consists in causing chlorine-gas to act on potassium ferrocyanide, the reaction being as follows:



This treatment may be carried on either in the moist or the dry way, but the latter method is very rarely used, the moist method being preferred. The operation is quite difficult to conduct, since it requires great care and attention. Practically it is carried on as follows:

A solution of potassium ferrocyanide indicating 26° B. is made in a copper boiler placed on a grate. This solution is transferred to a wooden vat, provided with a movable cover, into which a current of chlorine is conducted until the addition of a ferric salt no longer produces a precipitate in the liquor.

The saturation point is of extreme importance, for if too much chlorine be used there is formed a green precipitate of complex composition, to which the name of Berlin green has been given, and which prevents the ferricyanide from crystallizing, and besides, notwithstanding its insolubility, is extremely difficult to separate as it passes through the filters. On the other hand, if too little chlorine be used the ferricyanide obtained contains non-decomposed ferrocyanide.

Frequent tests are made by adding a ferric salt to a portion of the liquor, and when a precipitate is no longer produced, just at that point must the further addition of chlorine be stopped. In order to tell exactly the saturation point, the color of the solution should be examined by candle light, the end of the reaction being indicated by the fact that the solution being at first greenish becomes red. But this change in color, although quite distinct in dilute solution, is scarcely perceptible in concentrated solution. The testing should preferably be done with a ferric salt absolutely free from ferrous salts.

Stirring must be kept up continually during the addition of chlorine, otherwise the ferricyanide formed at certain points would be broken up under the prolonged action of chlorine, which would produce the above-mentioned green compound.

When the addition of chlorine is stopped, the solution is filtered and immediately transferred to a copper boiler similar to that in which the ferrocyanide was dissolved, and concentrated to 27–28° B. by continued boiling, for the crystals have a tendency to become deposited on the sides of the vat. When this point is reached the liquor is transferred to wooden vats or crystallizing vessels, where it is allowed to stand for five days. At the end of this time the mother-liquors are separated from the red prussiate crystals by decantation. These mother-liquors are subjected either to two further concentrations, to 28 to 29° B., or else they may be used in dissolving a fresh quantity of yellow prussiate which is to be subjected to the action of chlorine. When the conversion is complete the solution of ferricyanide is concentrated to 29° B. and left to crystallize. These new mother-liquors which are decanted are concentrated until they register 31° B. while hot; after which they are transferred into vats where the potassium chloride is precipitated. After standing six or seven hours, the liquors while still warm are decanted, and may again be used to dissolve ferrocyanide. The crude crystals of the four operations are then collected and dissolved in hot water in a copper boiler; the solution is concentrated to 27° B. while hot, and then transferred into wooden vats or crystallizing vessels, where they are left for several days.

As large crystals are commercially much more important, in order to obtain a beautiful crystallization, it is advisable to pour gently on

the surface of the solution about 20 litres of water, which floating on the surface prevents the formation of small crystals. When the crystallization is complete the mother-liquors are decanted, and may be used in dissolving a fresh quantity of crude crystals. They may thus be used five or six times provided they are not too heavily charged with potassium chloride. When this salt becomes too abundant the mother-liquors are concentrated in order to remove it by crystallization, and it is then sold as fertilizer.

The crystals of potassium ferricyanide are allowed to drain and then are dried upon flat iron plates gently warmed with waste heat. This treatment should preferably be conducted in a dark place, and be done as rapidly as possible in order to avoid too long contact with air.

In this way for 100 parts of yellow prussiate about 70 parts of ferricyanide are obtained, the theoretical yield being 77.9.

The process by the dry way consists in causing chlorine to act upon powdered ferrocyanide, placed in very thin layers in revolving apparatus or in chambers similar to those used in the manufacture of chloride of lime.

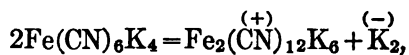
The ferrocyanide is first deprived of part of its water of crystallization in order that it may be powdered, as chlorine exerts but a slight action on the anhydrous salt; then it is ground with a grindstone, sifted, and subjected to the action of chlorine till absorption no longer takes place. The reaction is exactly the same as in the moist way: Ferricyanide and potassium chloride are formed which may be separated by crystallization. Quite often the product obtained in the dry way is sold just as it is when removed from the absorption apparatus, i.e., in the form of a powder consisting of a mixture of ferricyanide and chloride of potassium. Various other methods have been devised for the production of red prussiate.

**Reichardt's Process.**—Reichardt (1869) proposed replacing chlorine by bromine, while Kramer recommended digesting Prussian blue with potassium hypochlorite. Rodgers advised precipitating a solution of a mixture of 2 parts potassium sulphate and 1 part iron alum with barium cyanide, then to filter, concentrate, and crystallize. It is not known that these methods have been tried on an industrial scale.

The action of ozone or of ozonized oxygen has likewise been tried, the ferrocyanide being very rapidly converted into ferricyanide.

Electricity produces the same result. Two methods have been invented with a view to utilizing the electric current on ferrocyanide. These are the processes of the Société des Mines at Bouxvillers, and of Dubosc.

It is well known that under the action of the electric current passing through an aqueous solution of ferrocyanide, the latter is converted into ferricyanide which appears at the positive pole, while at the negative pole potassium is deposited, which, in contact with water, forms hydrogen and potassa,



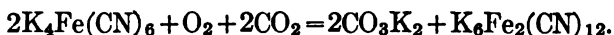
but it is likewise known that the action is reversible, the electric current converting ferricyanide into ferrocyanide. This phenomenon is explained by supposing that in the first case the ferricyanide is reduced by the hydrogen produced at the negative pole, while in the second case, the oxygen of the positive pole oxidizes the ferrocyanide. On the other hand, the prolonged action of the potassa converts a part of the ferricyanide into ferrocyanide.

**Process of the Mines at Bouxvillers.**—This process (French patent No. 176675, Oct. 15, 1886) aims at avoiding these very objections. The conditions under which the electric current should be conducted have been so carefully studied that there is no formation of Prussian blue, and the ferricyanide formed is not decomposed. The electrodes are placed in cells separated by porous diaphragms, the negative cell containing water, the positive cell being filled with a solution of potassium ferrocyanide.

If under these conditions an electric current of an electromotive force of 1.4 to 5.4 volts be conducted the ferrocyanide is converted into ferricyanide which is formed in the positive cell, whereas in the negative cell caustic potash is formed with the liberation of hydrogen. In this way the two solutions are separate, and the potash does not exert its injurious action on the ferricyanide, and thus a pure solution of ferricyanide is obtained, and it remains only to concentrate and to crystallize it.

The water of the negative cell may be replaced by mercury, in which case an amalgam of mercury and potassium is formed.

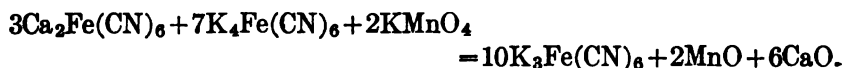
**Dubosc's Process.**—Dubosc (French patent No. 207193, July, 24, 1890) likewise uses the electric current in order to convert the ferrocyanide into the ferricyanide. The electrolysis takes place in the presence of sodium chloride. At the same time, or afterwards, a current of carbonic acid is passed through, which neutralizes the alkaline base and separates the ferricyanide formed from the carbonate and the chloride:



**The Process of the Deutsche Gold und Silber Scheide-Anstalt** (French patent No. 218246, 1891) has for its object the avoiding of the formation of soluble salts, which remaining in the solution together with the ferricyanide contaminate the latter, which often requires purification more or less costly.

It consists in using an alkaline-earth ferrocyanide, which after oxidation only leaves an insoluble compound. The oxidation is made more easily, it seems, and either the electric current or permanganate or any other oxidizing agent which does not leave behind any soluble compound may be used. In any case, the small amount of alkaline-earth base which dissolves may be precipitated either by sulphuric or carbonic acid.

Calcium ferrocyanide is preferred, in which case, when permanganate is used as the oxidizing agent, the reaction is as follows:

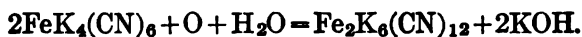


The oxid of manganese and the greater part of the lime, being insoluble, remain in suspension. By passing a current of carbonic acid, the small amount of dissolved lime is easily precipitated. After filtration an absolutely pure solution of ferricyanide is obtained, which may be concentrated and crystallized.

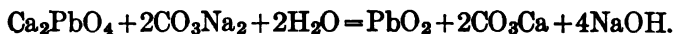
The process may likewise be applied to the chlorine method, the oxidation being more rapid and the yield greater than by the ordinary method. But this oxidizing agent leaving behind soluble compounds, pure solutions are not obtained, as is the case where the oxidizing agent leaves behind only insoluble impurities which may be easily filtered off.



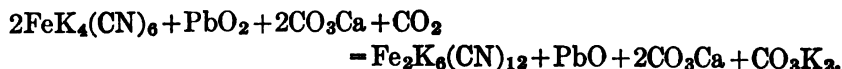
**Kassner's Process.**—This process (1893) is based on a reaction which was pointed out by Lunge in 1881. This investigator recommends the oxidation of ferrocyanide by means of lead peroxid and carbonic acid according to the reaction



Kassner, however, no longer uses peroxid of lead, but instead an alkaline-earth plumbate, e.g. calcium plumbate. This substance, the formula of which is  $\text{Ca}_2\text{PbO}_4$  or, better,  $\text{CaO}, \text{PbO}_2$ , possesses the peculiar property when in contact with even the weakest acids, such as carbonic acid and even carbonates and some other salts, of becoming converted into lead bioxid and the calcium salt of the acid used. Thus if calcium plumbate be heated with sodium carbonate at  $130^\circ$  under pressure, an insoluble mixture of chalk and lead bioxid is obtained, caustic soda being in solution:



Now then, if a mixture of chalk and lead bioxid be held in suspension in a solution of potassium ferrocyanide and a current of carbonic acid be conducted through it, there will be formed potassium ferricyanide, lead oxid, carbonates of lime and of potash, according to the reaction



By adding to the solution calcium ferricyanide, the carbonate of potash is converted into carbonate of lime, so that nothing remains in solution except potassium ferricyanide, which may be separated by filtration, concentration, and crystallization:



It is best to add the calcium ferricyanide after the oxidation with the lead salt, for the chalk formed in this second reaction may thus be collected, and so not hinder the recovery of the lead salt.

Calcium ferricyanide is obtained by the action of calcium plumbate on the corresponding ferrocyanide. A very intimate mixture of

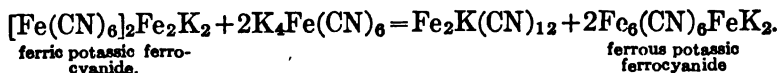
lead peroxid and chalk is thus made, and with a slight excess of this oxidizing mixture calcium ferrocyanide in concentrated solution, under pressure, is oxidized. The solution of calcium ferricyanide obtained may be directly utilized in the conversion of alkali carbonate.

**Carl Beck's Processes.**—These processes (German patent No. 15459, Nov. 28, 1893; No. 16088, May 4, 1894; No. 17677, May 22, 1895) are based on the action of persulphates, which are very energetic oxidizing agents, as is well known. The reaction is as follows:



Either the persulphate of ammonia or that of sodium may be used, but on account of the greater solubility of the former, it is preferred. A solution of potassium ferrocyanide is prepared by dissolving this salt in exactly its weight of hot water. When this solution has cooled to 60°, a solution of ammonium persulphate containing 540 grams of this salt per liter of water is slowly added. The reaction being very lively, heat is liberated to such an extent as to necessitate cooling the vessel in which the reaction is conducted. The neutral double sulphate of ammonium and potash, being but slightly soluble, is deposited on cooling. It is separated by decantation; the ferricyanide is then crystallized. On account of the relatively high cost of persulphates it seems improbable that this process should be used on a large scale.

**Williamson's Process.**—One process which has been somewhat spoken about lately and which had already been pointed out by Williamson, still remains to be mentioned. It consists in starting with the product known as soluble Prussian blue, a product which is obtained by precipitating iron sesquioxid with an excess of potassium ferrocyanide. The precipitate obtained is washed, the wash-water rapidly becoming blue, due to the presence of the compound  $[\text{Fe}(\text{CN})_6]_2\text{Fe}_2\text{K}_2$ , or ferric potassium ferrocyanide. When this product is treated with potassium ferrocyanide, it yields potassium ferricyanide and ferrous potassic ferrocyanide,



It is only necessary to digest the potassium ferrocyanide with a slight excess of potassium ferri-ferrocyanide, then to filter, evaporate, and allow to crystallize. The ferricyanide thus obtained is perfectly pure, and, as may be seen, the process requires neither great care nor complicated apparatus. There remains on the filter a mixture of potassium ferro-ferrocyanide and the excess of potassium ferri-ferrocyanide used. This latter product may be recovered and may again be used in the manufacture of a fresh amount of ferricyanide by treating it with nitric acid. The same amount of this product could thus be used indefinitely.

Notwithstanding its extreme simplicity we do not know if this process has been used industrially.

## CHAPTER IX.

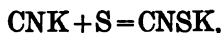
### MANUFACTURE OF SULPHOCYANIDES.

SULPHOCYANIDES, sulphocyanates, or rhodanates as they are sometimes called, are very little used in the arts. Yet, at one time they were very important industrially, for they were considered a very profitable source of manufacture as an intermediary product of cyanides. On this account their production was the basis of several processes about which the investigator and manufacturer should know. These processes, especially two of them, mark a real progress in the cyanide industry, and they will be minutely described as they deserve.

Before entering upon the study of the various methods for the manufacture of sulphocyanides, it will be well to briefly recall the different methods of obtaining these compounds.

Sulphocyanides may be produced:

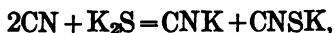
- (1) By the direct action of sulphur on a cyanide,



or on a ferrocyanide, either by boiling or by ignition.

- (2) By igniting nitrogenous substances with potassium sulphate, or with sulphur and potassium carbonate.

- (3) By the action of cyanogen, hydrocyanic acid, or cyanides on metallic sulphides,

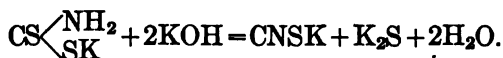


or by the action of hydrocyanic acid on a mixture of ammonia, sulphur, and ammonium sulphide.

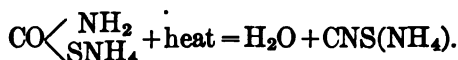
- (4) By the action of carbon bisulphide on ammonia on heating:



- (5) By the action of heat, or of alkalis on thiosulphocarbamates:



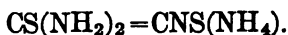
- (6) By the action of heat on ammonium thiocarbamate (Berthelot, Bull. de la Soc. chim. de Paris, 1868):



- (7) By the decomposition of fulminates by the aid of hydrogen sulphide:



- (8) By the action of water and heat on Thio-urea:



- (9) By the action of hot sulphuric acid on nitrogenous organic substances.

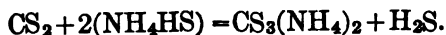
Of all these methods of preparation there is one which should be especially retained in mind, for it forms the basis of the methods of production of sulphocyanides on an industrial scale. That is the one which depends on the action of carbon bisulphide on ammonia.

**Gelis' Process.**—To Gelis, a Frenchman, belongs the honor of having applied this reaction to an industrial process.

This process is already old (1860), and it was put in operation for the first time in the inventor's own works at Villeneuve-la-Garenne.

It was carried on as follows, the operation comprising two distinct stages.

- (1) The action of sulphide of carbon on ammonium sulphide, with formation of ammonium sulphocarbonate:



- (2) Conversion of ammonium sulphocarbonate into ammonium sulphocyanide by heating it to 100° with potassium sulphide



The first stage takes place in an apparatus fitted up with a wide-bladed stirrer. The sulphocarbonate formed is transferred to a sheet-iron still together with potassium sulphide and the mixture is heated to 100°. The hydrogen sulphide and the ammonium sulphhydrate set free are condensed in a sheet-iron cylinder entirely surrounded with water, into which gaseous ammonia produced in another boiler is conducted, which is used in absorbing the hydrogen sulphide in order to form ammonium sulphhydrate, which, together with that produced in the decomposition of ammonium sulphocarbonate, is used in the manufacture. The condensation ends in a coil in sheet-iron boxes fixed up with compartments, and finally in bottles.

The sulphocyanide was then treated at 140–160° with reduced iron in deep wide pans made of cast iron and hermetically sealed.

In his report to the Imperial Commission of the Exposition at London in 1862, Gelis mentions the fact that his experiments have been carried on with more than 1000 kg. at one time, and that the raw materials are products easily found in the market. He adds that the manufacture is extremely easy

In the "Annales des Mines du Conservatoire des Arts et Métiers," 1862, page 55, Payen gives the net cost of ferrocyanide manufactured by Gelis' process, the cost being based on the production of 30,000 kg. potassium ferrocyanide.

Carbon bisulphide (crude).....	35,000 kg. @ 45 fcs. per 100 kg. ....	15,750 fcs.
Potassium sulphate. ....	36,400 " " 40 " " " ....	14,510 "
Ammonium sulphate.....	25,300 " " 35 " " " ....	8,875 "
Reduced iron.....	50,000 " " 10 " " " ....	5,000 "
Quicklime. ....	17,500 " " 4 " " " ....	700 "
Cost of converting the potassium sulphate into potassium sulphide, 3 fcs. per 100 kg. ....		1,092 "
Labor, 12 men @ 3.50 fcs. per day, 30 days. ....		1,260 "
Fuel. ....		600 "
Rent and general expenses for one month. ....		1,000 "
Losses of raw materials, etc., 15% of expenses. ....		7,322 "
		<hr/>
		56,139 fcs.
Deducting from the above one third of the potash in the form of carbonate. ....	5,000 fcs.	
25,000 kg. sulphur @ 13 fcs. ....	3,250 "	
	<hr/>	8,250 fcs.
Net cost for 30,000 kg. potassium ferrocyanide. ....		47,889 fcs.
or 1.59 fcs. per kilogram.		

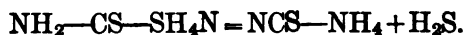
Gelis' process had but a short existence, as to-day it is entirely abandoned, because it is, in fact, rather difficult to operate it on a large scale. Besides, it should be remarked that only half of the ammonium sulphocarbonate is converted into potassium sulphocyanide at the time of the action of potassium sulphide, and, moreover, it requires costly and complicated apparatus.

Gelis' method was again taken up about 1878 by two manufacturers, A. de Günzburg and Tcherniac (French patents of Feb. 12, 1878, April 25, 1879, Dec. 24, 1880), who improved it remarkably. The process is as follows:

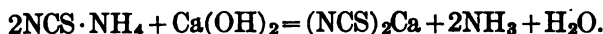
(1) Production of thiosulphocarbamate of ammonia by the direct union of carbon bisulphide and ammonia at 100° under pressure:



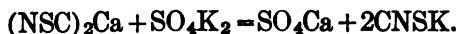
(2) Conversion of this salt into ammonium sulphocyanate by heating at 105°:



(3) The conversion of ammonium sulphocyanate into calcium sulphocyanate by distillation with quicklime, and the reproduction of half of the ammonia used in the reaction:



(4) The conversion of calcium sulphocyanate into potassium sulphocyanate by treating it with potassium sulphate:



(5) Conversion of the potassium sulphocyanide into potassium ferrocyanide with iron at 450° according to the reactions which we have already pointed out:



(The object of Tcherniac's process was the production of potassium ferrocyanide.)

As may be seen, the whole of these reactions forms a really complicated work, and difficult enough to carry on an industrial scale, although theoretically it appears quite simple. And it is only by reason of unheard-of efforts, of rare perseverance, and of long and patient investigations, which are all to the honor of Tcherniac and de Günzburg, that these two learned manufacturers succeeded in exploiting their process on a large scale.

The Campagnie Générale des Cyanures, which is exploiting the patents of Tcherniac and de Günzburg, operates in the following way in its works at St. Denis, the complete manufacture comprising five operations:

- (1) Preparation of ammonium thiosulphocarbamate.
- (2) Preparation of ammonium sulphocyanate.
- (3) Preparation of calcium sulphocyanate.
- (4) Preparation of potassium sulphocyanate.
- (5) Preparation of potassium ferrocyanide.

(1) *Preparation of Ammonium Thiosulphocarbonates*.—As has been seen, this product results from the action of carbon bisulphide on ammonia. The operation is carried on in a series of small autoclaves, forged iron boilers, tested to a very high pressure, and hermetically covered.

Each one of these autoclaves is provided with a thermometer, a manometer, a wide-bladed stirrer, and three tubulatures or cocks, one for the inlet of the solutions, the other for the exit of the gases which are produced, and the third for emptying the apparatus. They are encased in an exterior wrapper heated with steam. The reaction is conducted separately in each one of the autoclaves represented in Fig. 22. A pump *p* feeds the autoclaves with a mixture of carbon bisulphide, 20% ammonia, and ammoniacal liquors furnished by preceding operations.

When the apparatus has been suitably charged with this mixture the cock connecting with the pump is closed, and the stirrer is set in motion. Steam is admitted through the tube, *V*, and the whole heated till the thermometer registers 100°. At this moment the inlet of steam is stopped, and the stirrer is kept going till the pressure in the autoclave is 15 atmospheres; the operation may then be



considered finished. The product of the reaction is a mixture of ammonium sulphocarbonate, and carbon bisulphide in excess. The cock of the compressing tube, *C*, plunging to the bottom of the apparatus is opened, and owing to the effects of the high pressure in the autoclave, the mixture is violently driven into the still, *A*,

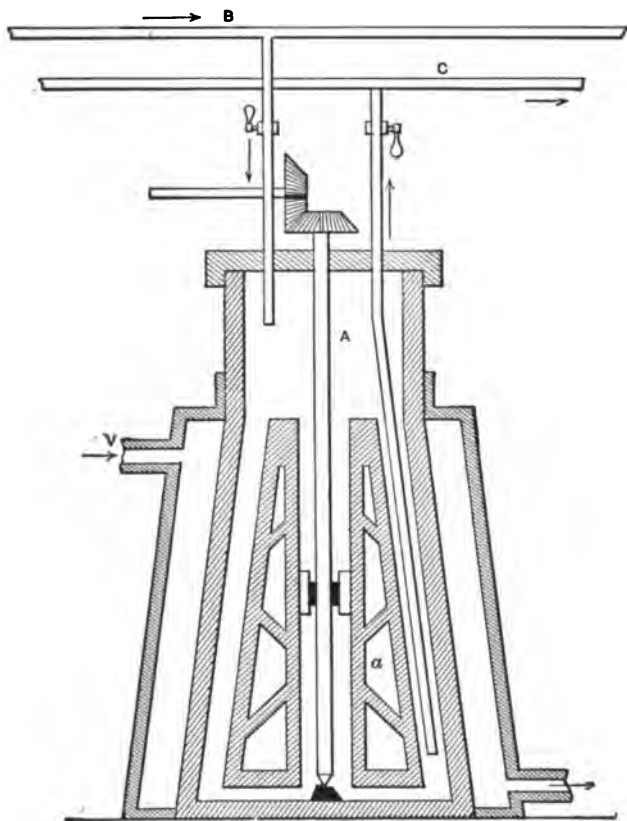


FIG. 22.

represented in Fig. 23, and in which the conversion of ammonium sulphocyanate takes place.

(2) *Separation of Ammonium Sulphocyanate*.—The still in which this precipitation is carried on consists of an ordinary boiler, heated to a temperature of 105–110° C. by means of a coil of steam placed at the bottom. Under these conditions the thiosulphocarbonate is decomposed in ammonium sulphocyanate and hydrogen

sulphide, while the remaining carbon bisulphide and ammonia distill. The still is surmounted with a cylindrical vessel, *B*, called an entrainment device, the object of which is to separate the gaseous products from the liquid products mechanically drawn over during the distillation. These latter come with the gaseous products through the tube, *b*, into the entrainment device, there they are condensed and returned to the still, *A*, through the tube, *c*, which plunges into the liquid to be distilled, while the gaseous products continue their course to the absorption apparatus.

This apparatus consists of two columns filled with pieces of coke, placed above a surface heat-exchanger, which is itself built upon a very large receiver, into which the products of condensation are col-

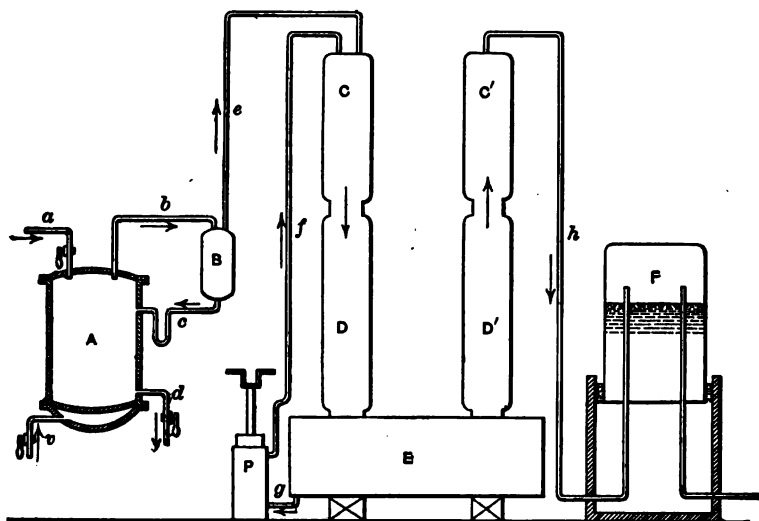


FIG. 23.

lected. A gasometer bell, whose capacity is about 15 cu. m., is used as a regulator, and at the same time holds back the residual gases of the condensation, consisting almost entirely of hydrogen sulphide.

The gases which emerge from the entrainment device and which consist of a complicated mixture of hydrogen sulphide, ammonium sulphide (obtained from the action of hydrogen sulphide on ammonia in excess), water-vapor, and carbon bisulphide, pass into the coke column, *C*, then into the exchanger, *E*, and are condensed in the

vessel, *R*. A pump, *P*, takes this liquid and transfers it through the tube, *f*, to the upper part of the coke column, where it is discharged in the form of a continuous shower which, while making sure of a complete condensation, prevents any stoppage which the deposits of ammonium sulphide might occasion.

The second column, *C'D'*, is used as a reflux condenser, and allows the last portions of the liquid, which might have escaped treatment to be collected.

Carried out in this way, the condensation is very imperfect; in fact, notwithstanding all the desirable improvements of the condensation apparatus, hydrogen sulphide always carries along an appreciable amount of carbon bisulphide, sometimes even 20% of the product used. Notwithstanding this, the inventors of this process have succeeded in preventing completely the disastrous effects of this contamination by making the hydrogen sulphide bubble through oil, preferably heavy petroleum oil. Under these conditions the carbon bisulphide only is absorbed by the oil, and it only requires a distillation to separate it and to revivify the oil, whereas the hydrogen sulphide escapes in an almost pure state. (Patent of May 31, 1881.) Thus carried on, this treatment, which is one of the finest examples of continuous operations, gives a large yield which may even reach 95% of the theoretical.

The ammonium sulphocyanate remaining in the still is discharged after the distillation through the cock *d*.

These first two operations of Tcherniac and de Günzburg's process require very strong apparatus. With the exception of the coil in the still, which is of tin or of aluminum, the apparatus should be of forged or of cast iron, which metals are known through experience to be the most suitable for this kind of work, in fact, in the presence of a slight excess of ammonium sulphhydrate, iron is sufficiently resistant. On the other hand, it is absolutely necessary that the coil should be of tin or of aluminum, for in this part of the apparatus the iron, no longer protected by the ammonium sulphide, would be attacked by a small quantity of free sulphocyanic acid, produced by the partial dissociation of ammonium sulphocyanide, ferrous sulphocyanate being formed which would contaminate the product and color it red; tin is but slightly attacked, and pure aluminum not at all.

If absolutely pure ammonium sulphocyanide is desired it will be necessary to carry on the operation in an aluminum apparatus. A still entirely of aluminum has been constructed, and the results obtained have been in all points entirely satisfactory.

At present a great deal of ammonium sulphocyanide is used in the preparation of aluminum mordants in dyeing, and the salts to be used for this purpose should be especially free from iron. In this case the manufacture is carried on in aluminum apparatus, and it is stopped at this point; the ammonium sulphocyanide which remains in the still is cleared out, evaporated at the temperature of 125°, and then allowed to crystallize in wooden vats lined with tin.

When the operation has been carried on in an iron still and the ammonium sulphocyanide thus obtained therefore contains ferrous sulphocyanide, which, in contact with atmospheric oxygen, is converted into ferric sulphocyanate and gives the characteristic red color of this latter salt, it is necessary, if it is desired to obtain a white salt capable of remaining white, to precipitate the ferrous salt with ammonium sulphhydrate or simply to subject the solution, to which a little ammonia has been added, to the action of a current of air, which precipitates the whole of the iron as peroxide. This is allowed to stand and then filtered and the solution evaporated in a tin boiler.

If, on the other hand, the object is to manufacture potassium ferrocyanide the operations which have been previously described are continued.

(3) *Preparation of Calcium Sulphocyanate.*—This is based on the following reaction:



The apparatus which is used for this treatment consists of a vertical boiler, or still (Fig. 24) heated by means of the steam coil, V. This coil surrounds a perforated sheet-iron basket in which lime is placed. Besides, this still or reservoir is provided with a thermometer and a diverter similar to that of the still just described. The lime having been placed in the basket the reservoir is charged with the solution of ammonium sulphocyanide, and the temperature raised to 125°. Under these conditions the reaction indi-

cated above is brought about and the ammonia set free is distilled. When no more ammonia distils over the reaction is considered finished, calcium sulphocyanate remaining in the reservoir. The ammonia distilled over is condensed in the following apparatus: On emerging from the still the ammonia passes into the diverter, whose object it is to separate the liquids from the vapors, a separation which is rather delicate, owing to the abundant froth produced by the solution of calcium sulphocyanate, but which is easily enough done in the entrainment device where the foam liquefies and flows back into the reservoir, whereas the ammonia continues its course reaching the exchanger, *C*, where it is partly condensed. The last

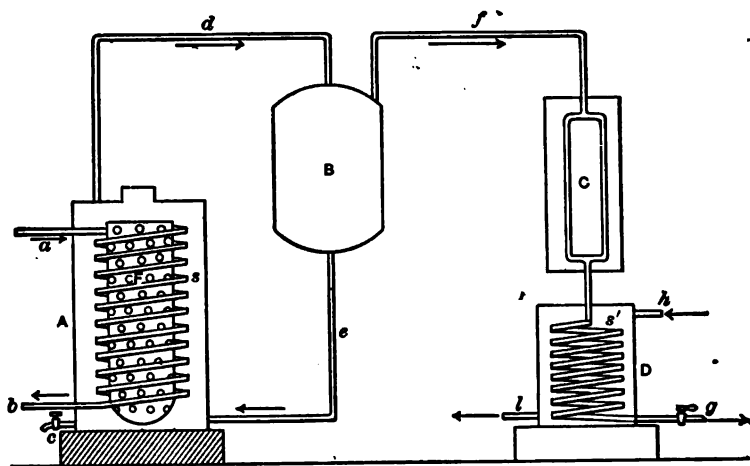


FIG. 24.

portions are held back in the absorber, *D*, cooled by a coil containing cold water. The amount of water which flows is so regulated that a 20% solution of ammonia is obtained, which may be used in the manufacture of ammonium thiosulphocarbonate.

The solution of calcium sulphocyanate which remains in the distilling-reservoir is removed through the cock, *C*, and then treated so as to convert it into potassium sulphocyanide.

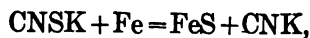
*Conversion of Ammonium Sulphocyanate into Potassium Sulphocyanate.*—This operation takes place in open cylindrical boilers heated directly by fire and fitted up with scraper-stirrers. First, a concentrated and boiling solution of potassium sulphate is prepared

in the boilers, so that the amount of this salt is somewhat greater than that which is exactly necessary for the conversion of the ammonium sulphocyanate. Then the calcium sulphocyanide is run in in small portions at a time, the stirrers being set in motion after each addition. Calcium sulphate is precipitated. The resulting mash is subjected to filter-presses in order to separate the calcium sulphate.

As the filtrate still contains some calcium sulphocyanate, undecomposed, the latter is precipitated with potassium carbonate, and after filtration the filtrate is evaporated at  $125^{\circ}$  and crystallized. Besides sulphocyanide of potash, this solution contains some sulphate, chloride and carbonate of potash, which latter salts crystallize first. These crystals are removed and the remaining solution is evaporated to dryness, this solution containing only potassium sulphocyanide. The residue is fused at  $300^{\circ}$  in deep, wide pans, made of cast iron, and thus yields a product as pure as possible.

It now only remains to convert the sulphocyanide into potassium ferrocyanide. Although the study of this preparation does not exactly belong to the scope of this chapter, and has already been discussed in a preceding chapter, a few words will be said, because of the fact that Tcherniac and de Günzburg's process has especially to do with the production of potassium ferrocyanide.

These investigators carry out this conversion as follows: The potassium sulphocyanide, as above obtained, is pulverized and intimately mixed with powdered reduced iron, or sifted cast-iron powder. The mixture is quickly introduced into metallic boxes with covers, A (Fig. 25), which are placed in a sulphur stove kept at a temperature of about  $450^{\circ}$ , the stove being heated directly over the fire. When the operation is finished the boxes are removed and placed in another stove hermetically sealed and surrounded with cold water, where they are thus cooled out of contact with air. The fused and cooled mass, consisting of a mixture of iron sulphide and potassium cyanide, according to the reaction



is treated with water, and yields a solution of potassium ferrocyanide containing 30–35% of this salt, which it is only necessary to purify by evaporation and crystallization.

This last part of Tcherniac and de Günzburg's process was for a long time the cause of the failure of the method. It was not until much feeling about and numerous investigations that these inventors succeeded in evolving the following conditions which assure the success for the method:

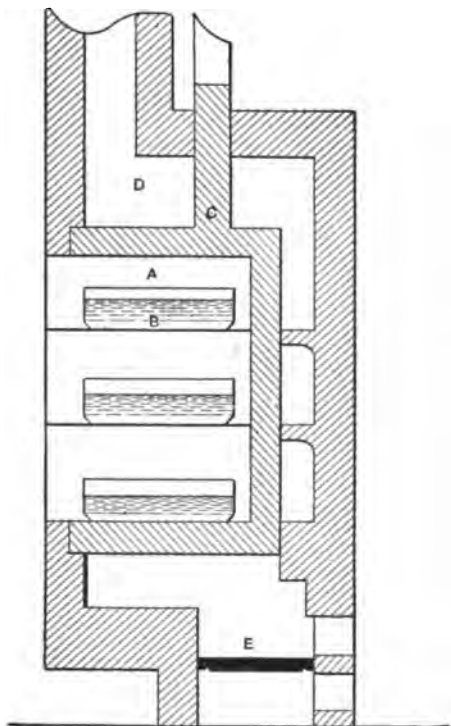


FIG. 25.

- (1) The sulphocyanate should be perfectly dry and pure.
- (2) The iron should be free from rust and impurities.
- (3) The mixture should be as intimate as possible.
- (4) The temperature of fusion should be  $450^{\circ}$ ; no higher than  $500^{\circ}$ , no lower than  $300^{\circ}$ .
- (5) The fusion and the cooling should take place out of contact with air.

If all these conditions are not strictly followed the results may be defective.

Such is the process of Tcherniac and de Günzburg; it occupies an important place in the history of the cyanide industry, and has given results truly remarkable; it is one of the few processes that has lived. Other manufacturers have been animated by the works and the process of Tcherniac and de Günzburg, which they have to some extent improved.

**Deiss and Monnier's Process.**—Thus it is that the Deiss and Monnier Company of Saint-Denis (Patent No. 217,825, Dec. 3, 1891; March 2, 1892) recommend preparing sulphocyanides by the action not of an aqueous solution of ammonia, but of gaseous ammonia on carbon bisulphide. According to these inventors, the reaction is more rapid, and larger amounts of raw materials may be treated in small and less complicated apparatus than that of Tcherniac's process. Moreover, the reaction takes place in the cold and at a normal pressure, which therefore requires less costly apparatus. The process is otherwise carried on as follows: The sulphide is mixed with rich carbides (petroleum, vegetable or mineral oils, higher alcohols, e.g., butyl or amyl, etc.), to the extent of 30 to 50%. By means of a pump this mixture is brought in contact with ammonium sulphide, the object of which is to dissolve the thiosulphocarbonate as fast as it is formed, the mixture being kept cold by means of running cold water. Ammonium thiosulphocarbonate is immediately formed. When the whole of the carbon bisulphide is combined, the solution of thiosulphocarbonate, separated from the carbide by decantation, is run into an apparatus which is heated externally by a coil of steam, where this salt is decomposed into ammonia and hydrogen sulphide, which are set free, and into ammonium sulphocyanide, which remains in the still. This latter solution is concentrated and allowed to crystallize. The hydrogen sulphide set free in this reaction is conducted into a washer containing oil, where it leaves behind the carbon bisulphide, which was entrained. Some ammonium sulphhydrate is likewise formed by the action of the gaseous ammonia on hydrogen sulphide, and this is collected in a receiver containing water.

The reaction pointed out by Millon and Gélis successively,



converts only half of the ammonia used in the reaction into cyanogen



compounds; the other half, to a large extent at least, being converted into ammonium sulphide and ammonium sulphhydrate. Now, then, the ammonium sulphide causes an enormous pressure inside the apparatus, which necessitates special appliances very costly and complicated.

Means of overcoming the serious objection of the formation of ammonium sulphide have therefore been sought. All the improvements to Gélis's reaction toward this end depend upon the same principle: The absorption of the hydrogen sulphide by a non-volatile base, which diminishes the pressure appreciably; since, for example, the pressure of calcium sulphhydrate at the boiling-point is not greater than that of water, whereas that of ammonium sulphide is about seven times greater (A. E. Wareing). Moreover, the ammonia is thus rendered free for the conversion into sulphocyanide.

**Hood and Salamon's Process.**—One of the first improvements along this line is that of Hood and Gordon Salamon. (English patent No. 5534, 1891, and German patent No. 12018, Feb. 27, 1892; Aug. 3, 1893). It consists in treating while hot, a mixture of carbon bisulphide and ammonia, in the presence of a mixture of lime and an oxidizing agent, such as manganese peroxide. ("For this purpose Weldon mud well washed in order to completely remove the calcium chloride may be taken"), or ferric oxid, etc.

The operation is conducted in a boiler autoclave, into which the mixture of lime and oxid of manganese is introduced, after which the apparatus is heated to 100°, when the carbon bisulphide and ammonia, mixed in molecular proportions, are added a little at a time. When the reaction is finished the product is taken up with water which dissolves the calcium and manganese sulphocyanates, leaving an insoluble residue of manganese sulphide and sulphur. These latter are separated by filtration; from the residue the manganese dioxide is revived and again used. The filtered solution is treated with an alkali carbonate in order to precipitate the lime and manganese and to convert their sulphocyanates into alkali sulphocyanate. This precipitation is fractionated, the manganese having a greater affinity for the carbonic acid than the lime has; and so manganese carbonates separates out first.

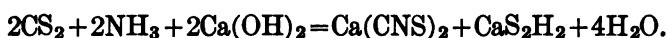
**Brock's Process.**—Somewhat similar is the process of J. Brock, A. E. Hetherington, P. Hurter, J. Raschen (English patent No. 21451, Nov. 1893; Dec. 1894). In the course of their researches on this

important question these chemists noticed that the presence of manganese and iron oxides was superfluous, and that the lime alone sufficed. Their process consists, therefore, in heating in a cylindrical apparatus, made of cast iron or steel and placed horizontally, a mixture of carbon bisulphide, ammonia, and lime in the following proportions:

Carbon bisulphide.....	100 parts
Slaked lime.....	200 "
Ammoniacal solution containing.....	45 "

dry ammonia-gas, together with a sufficient amount of water to make the mass fluid.

The amount of ammonia used is twice that required by the equation



The cylinder has double walls, steam circulating between the walls, bringing the temperature of the interior and its contents to 100° C. The cylinder is provided with a mechanical stirrer, which allows the mass to be continually stirred during the reaction, lasting from 2 to 6 hours. The same bottom through which the stirrer passes is provided also with a safety-valve, an outlet tube for drawing off, and a lid for the charging. A thermometer and a manometer allow the temperature and pressure to be watched.

After driving off the excess of ammonia by distillation the whole is filtered in order to remove the lime, and carbonic acid is passed through the product. Under these conditions the calcium sulphide and the calcium sulphhydrate are decomposed, hydrogen sulphide is set free and driven off, and carbonate of lime is precipitated. After filtering there remains a solution of calcium sulphocyanide which may be treated by any of the appropriate methods for its conversion into alkali sulphocyanide.

**Process of the British Cyanide Company.**—This process (German patent No. 14611, April 16, 1894; Jan. 10, 1895) consists, likewise, in causing ammonia to act on carbon bisulphide in the presence of a base, such as lime, without the use of any oxidizing agent. The apparatus used, a double-walled autoclave cylinder provided with a stirrer, differs but little from that of the preceding process. It

is first charged with 17-18.5 parts of an ammoniacal solution containing 7.15% dry gas, 101-102 parts hydrated lime, finely powdered, containing 72-75% CaO.

These two substances are intimately mixed and then are added 76 parts carbon bisulphide; the autoclave is closed and heated gently, the stirrer being kept in motion, when the manometer indicates 2 atmospheres pressure the heating is discontinued; the pressure continues to rise up to 6 atmospheres, when it falls.

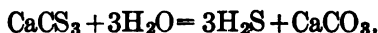
At this point the heat is again applied till the temperature of 115-120° is reached, and this is maintained for several hours.

As in the preceding process, the product of the reaction is treated with carbonic acid which displaced hydrogen sulphide from the calcium sulphide and the calcium sulphhydrate. The carbonate of lime is separated by filtration, the filtrate which contains only sulphocyanide being treated with an alkali salt which thus yields alkali sulphocyanide on evaporation and crystallization. The first part of the evaporation takes place in a distilling apparatus in the presence of caustic soda, and at boiling temperature in order to recover the small amount of ammonia remaining in solution (about 5%). The hydrogen sulphide set free may either be burned in order to yield sulphurous acid to be used in feeding the lead chambers, or else treated in the ordinary way for the extraction of sulphur from it. Conroy, who has made a whole series of investigations on these processes, clears up this subject considerably in an interesting paper in *The Journal of the Society of Chemical Industry* (1896). From the investigations conducted by this English savant, in collaboration with Zahortki, it follows that:

(1) An excess of ammonia is absolutely indispensable to carry on the reaction properly, as it is well known that in this reaction thiocarbonate of lime is also formed,



which in contact with water gives



unless there is an excess of ammonia, and in this case the reaction becomes

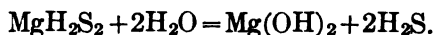
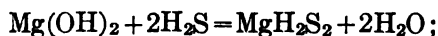


(2) The addition of lime does not exert any influence on the yield of sulphocyanate; it serves only to diminish the pressure.

(3) Carbon bisulphide and calcium sulphide unites in order to form soluble calcium sulphocarbonate, and this union is best made at the temperature of 50–60°.

(4) The solution of calcium thiocarbonate may be converted quantitatively into sulphocyanate; but in order to obtain a favorable yield it is necessary to work under pressure and in the presence of a large excess of ammonia.

**Albright's Process.**—A later improvement along this line, is that brought about by G. S. T. Albright, at Birmingham (German patent No. 4324, May 4, 1895; October 21, 1895). It consists practically in making use of magnesia instead of lime. Under pressure, magnesium hydrate fixes hydrogen sulphide, which is set free by the action of carbon bisulphide on ammonia in order to form magnesium sulphhydrate; and this salt again liberates hydrogen sulphide on boiling, while at the same time magnesium hydrate is reproduced and may be used for the next operation:



The operation is carried on in a boiler provided with a stirrer where magnesium sulphocyanide is at the same time produced. It is well to add to the magnesia a sufficient quantity of lime to fix completely the sulphocyanic acid formed. The insoluble magnesium hydrate is separated by filtration from the calcium sulphocyanide, which latter is then converted into alkali sulphocyanide by double decomposition with an alkali sulphate or carbonate.

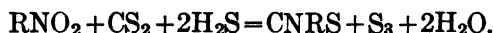
**Tcherniac's Process.**—Another class of methods for the production of sulphocyanides makes use of nitrites, carbon bisulphide, and hydrogen sulphide. Such are the processes of Tcherniac, Goerlich and Wichmann. This process had already in 1856 been pointed out by Schlagdenhaufen, who had observed that by heating carbon bisulphide and a nitrite in a closed tube there were formed sulphocyanate, carbonic acid, and hydrogen sulphide, but that under these conditions a large portion of the carbon bisulphide burns with the formation of sulphuric and carbonic acids, and at the

same time a large part of the nitrogen was lost as free nitrogen or in the form of nitrogen protoxide. If, on the contrary, as is done in Tcherniac's process, a mixture of carbon bisulphide, nitrite, and hydrogen sulphide be heated in an autoclave an almost quantitative yield of sulphocyanide is obtained.

Tcherniac's process consists (French patent No. 248163, June 14, 1895; Oct. 16, 1895) in heating the following mixture in an autoclave provided with a mechanical stirrer:

Nitrate of the base used. . . . .	1 molecule
Carbon bisulphide. . . . .	1     “
Hydrogen sulphide. . . . .	2 molecules

The hydrogen sulphide may first be made to act on the nitrite, or else be compressed into the autoclave, which is heated to 150° C. until the manometer indicates a depression, which shows the end of the reaction. This may be expressed thus:

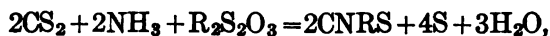
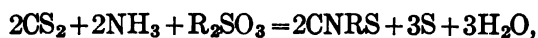


In order to make use of the whole of the nitrite the hydrogen sulphide should be in slight excess. The sulphur separates from the aqueous solution of the sulphocyanide, in the form of a crystalline crust, very easy to remove, and the sulphocyanide obtained is almost pure, and may be used for any purpose in the arts.

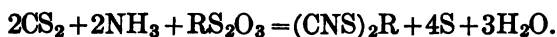
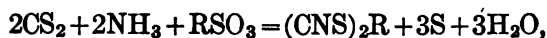
**Goerlich and Wichmann's Process.**—This process (German patent No. 9831, June 7, 1895; July 30, 1896) is identical in every respect with that of Tcherniac's.

Finally, it only remains to mention Goldberg and Siepermann's process (German patent No. 9494, Jan. 14, 1895; June 13, 1895). It consists in heating under pressure a mixture of carbon bisulphide, ammonia, and alkali- or alkaline-earth sulphite or bisulphite. The reaction which already begins at 100°, goes on actively at 120 to 130° by stirring constantly, and especially if the operation is carried on in the presence of an alkaline-earth sulphite.

In a general way the reactions may be expressed by the following equations in the case of an alkaline base:



or in the case of an alkaline-earth base (lime, magnesia),



The sulphur thus formed is collected as fast as it is formed under the solution of sulphocyanide in the form of a fused mass.

## CHAPTER X.

### MANUFACTURE OF PRUSSIAN BLUE AND VARIOUS OTHER COMPOUNDS.

PRUSSIAN blue, or ferric ferrocyanide, was, as we have already mentioned, the first cyanogen compound known. Its discovery occupies a very important place in the history of chemical industry, for it is in consequence of this happy finding that all the cyanogen compounds were produced.

The discovery of Prussian blue dates back to the year 1710, and like that of many chemical products it was due purely to chance. A Berlin manufacturer of colors, named Diesbach, wishing to precipitate cochineal lake by means of potash, and not having any of this substance on hand borrowed some of a pharmacist of that city, Dippel by name. This pharmacist gave him some potassium carbonate which he had used in rectifying an empyreumatical oil, of animal origin, of the same name. When Diesbach made use of this product, instead of the red lake which he wished to prepare, he obtained a magnificent blue precipitate. Surprised at this extraordinary phenomenon he took Dippel into his confidence, who was not slow in suspecting that this precipitate was due to the action of potash on iron alum, which Diesbach had used. In fact, on repeating the experiment Dippel obtained an absolutely similar result. From that time he resolved to make something out of this remarkable discovery. In a paper which he presented to the Academy of Berlin in 1710 he calls attention to this body, without however disclosing the mode of preparation, and he joined with Diesbach in the manufacture of this new product. The method of manufacture was kept secret till 1724, at which time an English chemist, Woodward, member of the Royal Society of London, succeeded in reproducing Prussian blue, and made public the method

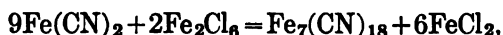
of preparation. This publication created a great sensation at the time, for with the exception of indigo no other blue coloring-matter was known. Woodward's method, practically unchanged, is the one carried on to-day in the works where Prussian blue is prepared.

It was begun by preparing a "blood-lye" obtained by treating with hot water the product of ignition of dried blood or other organic materials in the presence of potassium carbonate. This lye was then exposed to air in shallow pans until a lead salt gave no longer a precipitate, and then treated with a mixed solution of alum and copperas. The whole was constantly stirred with a stick, a brisk effervescence taking place, while at the same time a greenish precipitate was formed. It was allowed to stand for some time, and then decanted, the precipitate being washed with water until it had acquired a blue color. It was then drained, compressed in the form of cubes which were allowed to dry in the open air by means of gentle heat.

Prussian blue is also formed when ferrocyanide of potassium or barium or ferrohydrocyanic acid is precipitated by means of a salt of iron peroxide, or when potassium cyanide is precipitated by a ferro-ferric salt:



It is formed by the action of hydrocyanic acid on ferro-ferric-hydrate, or of a ferric salt on ferrous cyanide,



or by the action of an oxidizing agent, such as chlorine-water on ferrous cyanide, hydroferrocyanic acid, ferro-potassic-cyanide.

The best method of obtaining a splendid quality of Prussian blue is to precipitate potassium ferrocyanide with an acid solution of sulphate of iron protoxide (ferrous sulphate, green vitriol, copperas). This is done in the following manner:

Potassium ferrocyanide and ferrous sulphate are separately dissolved in 15 times their weight of water, or else a solution of each is prepared by dissolving 6 parts of the salt in 15 parts water. The solutions are then mixed, and while constantly stirring, a mixture of 1 part concentrated sulphuric acid and 24 parts fuming hydrochloric acid is added.



A grayish-white precipitate of ferro-potassic-ferrocyanide is formed, the mother-liquors containing potassium sulphate which may be removed by evaporation. The precipitate is allowed to stand several hours, and then it is washed with a large amount of water. It remains only to make it blue, i.e., to oxidize it. Under the influence of atmospheric oxygen or of any oxidizing agent, the ferro-potassic-ferrocyanide is, in fact, converted into Prussian blue:



As may be supposed, many methods have been used in the oxidation of ferro-potassic-ferrocyanide.

First, air was used. This is the oldest method, and the one which gives the poorest results.

Solutions of clarified hypochlorite of lime have likewise been much used, this solution being added in small quantities at a time. But although this process has been used a long time it has the objection of forming calcium sulphate, which is only slightly soluble together with the Prussian blue, which former, in mixing with the Prussian blue, weakens the color just so much, or at least forms white spots in the blue which depreciates the value.

In his " *Traité de Chimie appliquée aux Arts industriels* " Girardin gives a formula for making Prussian blue by means of hypochlorite of lime. The work is carried on as in the preceding, by precipitating copperas with prussiate in the following proportions:

Crystallized ferrocyanide. ....	10 parts
Copperas. ....	11 "

The precipitate formed is treated with hypochlorite of lime:

Chloride of lime dissolved in 100 parts of water. .... 1.5 parts  
and then with weak hydrochloric acid:

Hydrochloric acid diluted with 100 parts of water. .... 5.0 parts

Aqua regia at ordinary temperature and chromic acid have also been used, both of which methods have been abandoned, the first being too costly and the latter being objectionable on account of its leaving chrome alum, which is of little use, in the mother-liquors. In the latter case, the treatment was carried on as fol-

lows: A solution of 10 kg. of bichromate of potash in 100 liters of hot water was made; after cooling, 135 kg. of sulphuric acid (com.) was added, and this mixture was gradually poured on the white precipitate potassic ferro-ferrocyanide, which was diluted with boiling water until the precipitate had acquired a beautiful intense-blue color.

A boiling solution of potassium chlorate may profitably be used, but the best procedure is that which consists in using a warm solution of iron perchloride or of ferric sulphate. When this solution acts on the white precipitate, it is brought back to the state of proto-salt, which may then be treated with ferrocyanide and be used anew.

Whether the oxidation of ferro-potassic-ferrocyanide be carried on by one or other of the above methods, the conversion into Prussian blue is never complete, for another part of the white precipitate produces a compound which is also blue, and which seems to be a ferri-potassic-ferricyanide.

Although the preparation of Prussian blue seems at first sight very simple, it nevertheless requires care if a pure product of beautiful shade is to be obtained. The essential conditions which apply to all the methods just described are the following:

(1) The iron solution should always be poured into the potassium ferrocyanide and never the reverse, if it be not desired that the precipitate formed should enclose a large quantity of potassium ferrocyanide. (2) It is well to digest the Prussian blue with hydrochloric or nitric acid in order to remove the iron oxid completely, which always reduces more or less the intensity of the color.

The iron salt used should be as pure as possible, and especially should not contain copper, since the salts of this metal with ferrocyanide give a reddish precipitate which injures the brilliancy of the tint.

In the preparation of ordinary commercial Prussian blues, alum in various amounts is very often added at the moment of the precipitation. The alum salt forms aluminum ferrocyanide, which has the gelatinous appearance of aluminium, it being intimately mixed and held in the Prussian-blue precipitate, increasing the weight without appreciably injuring the tint, unless too great amounts are used.

The alum is added in various amounts according to the quality of Prussian blue desired. For pure blues, not any is added.

For a fine quantity of blue, one part of alum is used for three or four parts of ferrous sulphate; for an ordinary blue, one part to two or three of iron sulphate; and for blues of inferior quality, equal parts of the two salts. In certain blues of very low quality, as much as three parts of alum are used for one of ferrous sulphate.

Moreover, the varieties of Prussian blue are very numerous, and the quality of this product depends altogether on its mode of preparation. There are fifteen or twenty classes of Prussian blue, all differing from one another in their composition and color. The principal ones are: Berlin blue, Prussian blue of Paris or Milori blue, Paris blue, fine and dark, ordinary deep blue, and mineral or Antwerp blue, to which oxid of zinc or magnesium carbonate is often added.

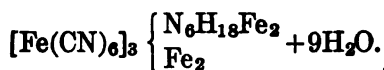
**Soluble Prussian blue.**—This compound, whose exact composition is not yet known, and which according to some is a union of ordinary Prussian blue and potassium ferrocyanide, and according to others a ferricyanide of iron and of potassium, is formed when a salt of iron peroxid (iron perchloride) is precipitated by potassium ferrocyanide in excess. The precipitate thus formed is a very beautiful blue insoluble in the solution containing potassium ferrocyanide, but soluble in pure water.

It is likewise obtained when a solution of iron iodide containing an excess of iodine is poured into a concentrated solution of potassium ferrocyanide (Reade). The blue precipitate thus formed is entirely soluble in water, even after drying.

**Turnbull's blue.**—Turnbull's blue is really a ferrous ferricyanide,  $\text{Fe}_5(\text{CN})_{12}$ . Its tint is still a more beautiful blue than that of Prussian blue. It is obtained by gradually pouring a hot solution of potassium ferricyanide, free from ferrocyanide, into a solution of a ferrous salt. This should be allowed to stand some time in the presence of an iron salt, if it be desired to obtain a product free from potash. It may be distinguished from ordinary Prussian blue by treating it with a hot potash solution, when it yields a precipitate of ferro-ferric hydrate and yellow prussiate, whereas Prussian blue gives ferric hydrate.

**Monthiers' blue, or ammoniacal Prussian blue.**—This compound,

which is more stable than ordinary Prussian blue, is a ferric iron and ferric ammonium ferrocyanide, its formula being



Monthiers obtained it as follows: An ammonia solution is poured into a pure solution of iron protochloride, the precipitate is rapidly filtered, taking all precautions to avoid contact with air, and the filtrate is gradually poured into a solution of potassium ferrocyanide. A white precipitate which becomes blue on contact with air and also a precipitate of ferric hydrate are formed. By treating with ammonium tartrate for several hours at 60–80°, the ferric hydrate may be removed, the ammoniacal Prussian blue being insoluble. This is washed with water.

**Antimony blue.**—This is nothing more than a Prussian blue of a beautiful shade, obtained in a special way, and falsely called antimony blue, as it contains no trace of this metal. It is obtained by boiling with potassium ferrocyanide the white precipitate formed when a tartar emetic solution is treated with concentrated hydrochloric acid; the blue precipitate formed is repeatedly treated with hydrochloric acid in order to remove the antimony completely. The antimony salt seems, therefore, to play no part except to facilitate the formation of this compound.

## PART FOUR.

### THE USE OF CYANOGEN COMPOUNDS.

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FORMERLY the cyanide industry owed its importance to the use of Prussian blue and of potassium ferrocyanide. Potassium cyanide had but limited application in medicine, in photography, in laboratories (as a reagent), and in the art of gilding and electrotyping. The chemical industry was therefore interested in the production of the first two compounds. To-day the reverse is true, Prussian blue finds but limited uses, 50% of the potassium ferrocyanide products being converted into potassium cyanide, and of all the cyanogen compounds the latter is the one most in use.

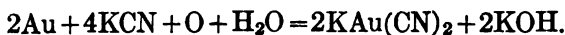
It has already been mentioned that the chief application of this salt is in the extraction of gold from its minerals, and it is due to this one use, which has become of considerable importance, that the industry of cyanogen and its compounds owes its present development.

Although the question of the treatment of gold minerals belongs rather to a metallurgical treatise, we must, however, mention the subject on account of its importance and the close bonds which unite it with the cyanide industry.

In fact, the methods for the extraction of gold by means of potassium cyanide have been considerably extended, and are destined still to increase and to become universal. The results thus far obtained are most satisfactory as well from an economical standpoint as from the standpoint of the yield, and there is no doubt as to the future.

The idea, which is the basis of these processes, is old. The solubility of gold in potassium cyanide has long been known. Faraday

observed this fact, later Prince Bagration did the same. But to Elsner belongs the honor of being the first to study the conditions under which the solution takes place. This investigation showed that oxygen was essential:



This theory was vigorously combatted by MacArthur and Forest, who were the first to think of applying this reaction to the extraction of gold on an industrial scale; but to-day it is an accepted fact that the solution of gold in potassium cyanide cannot take place without the help of oxygen, and is facilitated by the presence of any oxidizing agent (peroxides of sodium, barium, lead, manganese, permanganate, bichromate, nitrates, chlorate, potassium ferricyanide).

Furthermore, Christy (Jr. Soc. Chem. Ind., 1898, p. 332) has shown that the presence of free cyanogen and potassium cyanide is absolutely indispensable, the former being used in the formation of gold cyanide, which with the latter forms a soluble double cyanide.

As may be seen, the amounts of oxygen and of cyanide of potassium essential to the solubility of gold are very small. If the above equation be considered

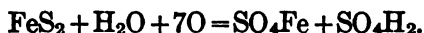


it will be noticed that 130.4 parts of potassium cyanide by weight dissolve 196.8 parts of gold, i.e., approximately 2 parts of cyanide to 3 parts of gold. As to the oxygen, only 15.96 parts are required to dissolve 396.6 parts of gold, i.e., 1 part oxygen to 25 parts precious metal. This oxygen is furnished in more than sufficient quantity by the amount of air occluded in the minerals and by the oxygen dissolved in the water used in the preparation of cyanide solutions.

In practice, the amount of cyanide used is always somewhat larger than that required theoretically, because the losses which occur during the "cyaniding" must be taken into account. The causes of these losses have been carefully studied by Ch. Butters, Clennell, and Mosenthal (Engineering and Mining Journal, Oct. 1892), and may be thus set forth:

(1) The oxidation of the auriferous minerals, the result of which is the precipitation of a part of the potassium cyanide in the

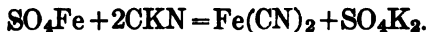
form of Prussian blue. The auriferous minerals now being worked in South Africa almost always contain iron pyrites, which latter, under the double action of air and of atmospheric moisture become oxidized, thus converting the mineral into the form of "free milling," as it is called in the Rand, with formation of iron sulphate and free sulphuric acid:



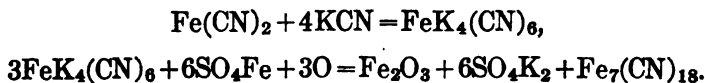
As the oxidation continues there are formed insoluble basic sulphate and insoluble ferric sulphate:



If, therefore, a mineral of this kind partially oxidized be placed in the presence of a cyanide solution the ferrous sulphate slowly acts on the potassium cyanide, forming cyanide of iron and potassium sulphate:

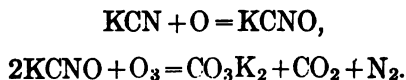


But in the presence of a large excess of potassium cyanide, the iron cyanide becomes in its turn converted into potassium ferrocyanide, which, in contact with ferric salts, yields Prussian blue:

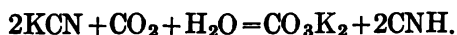


This conversion may be appreciably avoided by adding caustic soda or lime in order to saturate the free acid, but nevertheless there is always a partial conversion of cyanide into ferrocyanide.

(2) The action of the oxygen of the air on cyanide solutions. As is well known, the cyanides are very oxidizable salts, the action of air converting them, first into cyanate and then into carbonate:



(3) The action of carbonic acid of the air on the cyanide solutions:



(4) The action of metals other than gold existing in the minerals. The cyanide exerts its action on these metals, among which are most frequently met: copper, arsenic, zinc, nickel, cobalt.

A. W. Warwick has studied the solubility of gold in potassium cyanide, and from an article published in the Engineering and Mining Journal, June 29, 1895, the following conclusions are drawn.

(1) The presence of oxygen is an important factor for the solubility of gold in potassium cyanide.

(2) The solubility increases with the temperature. This fact explains why better results are obtained in warm countries than in those where the climate is subject to temperature variations.

(3) For a given time strong solutions are more active than dilute ones.

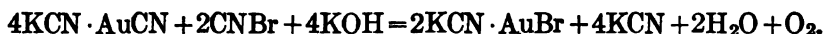
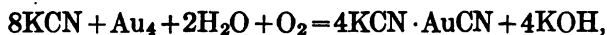
(4) Zinc exerts a prejudicial action. It becomes precipitated on the gold and causes the action of the cyanide gradually to cease.

(5) Copper likewise exerts a decomposing action, but much slower.

(6) The presence of gold chloride much increases the solubility, whereas potassium chloride exerts no action,



which means that the chloride, bromide, and iodide of cyanogen exert a favorable action on the dissolving power of potassium cyanide. But, according to the author, this action is only indirect, and the rôle of the halogen elements consists only in setting free the oxygen necessary for the solution of gold in the cyanide:



This formation of gold-bromine-cyanide of potassium is quite probable. (Lindbom has, in fact, obtained this compound.)



(7) The gold-silver alloys dissolve less easily in potassium cyanide, than does pure gold.

(8) Gold dissolves less easily in ferrocyanide and sulphocyanide of potassium than in the cyanide.

Having given these preliminary principles let us pass to the work of the extraction of gold by the said cyanide processes. To McArthur and Forest belongs the honor of having had the idea of utilizing the dissolving power of cyanide of potassium. Their process consisted in treating a mineral with a dilute solution of cyanide, then to precipitate the gold out of this solution by means of strips of zinc. As will be seen this process has been much improved, either by its authors or by other investigators. The treatment of gold minerals comprises two essential parts:

(1) Solution of the gold in the cyanide.

(2) Precipitation of the gold from these solutions.

*Solution.*—The cyaniding processes are especially used in the Transvaal in the Wittwatersrand, or Rand district as it is most generally called. It is known that the gold in the Transvaal minerals occurs in a very finely divided condition, which makes amalgamation very difficult; it is quite different, however, with the process of cyaniding, which may be carried on all the more easily the more finely divided the gold occurs.

As the mineral is brought out of the mines it is subjected to the first sorting, this being done on an inclined plane, the object being to remove most of the quartz and foreign matters. A second picking, by hand, by means of a current of water removes the gangue. It is then crushed, ground, and amalgamated. These two operations are carried on simultaneously in mills containing mercury. The amalgam thus formed is filtered under pressure, then distilled in retorts, the mercury being driven over while the gold remains behind. The non-amalgamated portion or pulp containing an appreciable amount of gold is treated with a current of water; then it passes over porous-copper amalgamating plates where a fresh quantity of gold is deposited. The pulp is then concentrated, yielding what is called concentrates. In this operation two classes of residues are obtained: The heavy residue, called tailings, the lighter, called slimes. The tailings and the slimes are important residues, reaching 60-70%

of the mineral at the Rand; the former contains 7-10 grams of gold per ton, the latter 4-7 grams.

It is especially these residues which are treated with potassium cyanide in order to extract the gold left from the amalgamation. However, the mineral may thus be treated directly.

Before touching upon the treatment either of the mineral, the tailings, slimes, or concentrate, the following four points should be carefully brought out by analyses concerning these substances:

(1) The gold-content, so as to know the amount of potassium cyanide to be used.

(2) Whether the mineral or the tailings contains the gold in a finely divided state, or in large grains; this will indicate the length of treatment with the cyanide solution.

(3) Whether the mineral or the tailings be acid or neutral.

(4) Whether the mineral or the tailings contain an appreciable quantity of metals other than gold and silver, having some affinity for cyanogen.

The auriferous materials will be treated according as they have one or other of the above characteristics. These points having been clearly established the treatment of minerals or tailings may be undertaken. The tailings are transferred to large lixiviating vats, sometimes made of wood or brick or cement, and sometimes of mortar, and rectangular or cylindrical in form, whose dimensions vary according to the works.

At the works of the African Gold Recovery Company where the processes of McArthur and Forest are exploited, the vats are wood, cylindrical in shape, 13 meters in diameter and 2.4 meters deep, with a capacity of 350 tons of mineral.

The Langlaate Estale Company and the Block Brick Company use circular vats of brick 12 meters in diameter and 3 meters deep, containing 400 tons of mineral.

At the works of the Crown Reef Company the vats are rectangular, of brick and cement, 12 meters long, 11 meters wide, 3 meters deep.

The vats of the Durham-Rondepoort Co. and of the Simmer and Jack Company are circular, made of wood; the former being 12 meters in diameter and 2.1 meters deep; the latter 12.6 meters in diameter and 4.2 meters in height.

At Robinson's works smaller circular vats are in use, holding only 75 tons of mineral, while at the new Primrose works, the lixiviating vats are very large and capable of holding more than 400 tons of mineral.

When wooden vats are used it is customary to cover the interior with a layer of paraffine or of a coal-tar and asphalt compound, experience having shown that the wood retains an appreciable amount of gold.

The filtering-vats, the use of which is becoming general, are provided with a false bottom, consisting of a wooden framework made of laths covered with a mat of cocoa fibers, or a double mat of jute, or a layer of jute and one of coca fiber, and sometimes even with quartz fragments. These vats are also provided with a two-branched drainage-pipe; one for dilute and the other for concentrated solutions.

Side gates or sluices are used in discharging the mineral after its treatment with cyanide.

First, the vats are filled with the mineral up to within 4 or 5 cc. of the top, the contents carefully leveled and the cyanide solution run in. This solution is generally prepared by dissolving the cyanide in a small amount of water in a small wooden vat, and then diluting this solution to the required strength.

When acid tailings are being treated, as is most generally the case, the neutral minerals having been almost completely used up, they should first be washed with water in order to remove the soluble salts, or "cyanicides" as they are called. This washing is done economically only when the analysis of the tailings or mineral shows a large amount of soluble salts. In some works, this is carried on in the cyaniding-vats themselves; but this is a very defective mode of treatment for these vats always retain on their walls a certain amount of cyanide, arising from a previous operation; this salt dissolves some of the gold and as these wash-waters are rejected it follows that there is a loss of precious metal. It is therefore better to do the washing in special vats, after which the mineral or the tailings are transferred to the cyaniding-vats. This washing is sometimes followed by another, this time using a caustic soda solution, containing 125 grams per 1000 liters of water, but it is generally better to mix the acid mineral with a certain amount of

powdered lime before charging the cyaniding-vat, the amount of lime naturally varying with the quantity of cyanicides present in the mineral (1 kg. per ton of very acid tailings or 250 grams per ton of tailings just from the battery). This method is more economical than that of caustic soda; lime is cheaper, and no special vat is necessary, the operation being carried on in the cyaniding-vats. The results obtained are also better; by using soda the charged solutions become turbid and befoul the zinc which later is to be used for the precipitation of the gold, whereas with lime the solutions remain perfectly clear.

When the mineral has been washed or treated with lime and been transferred to the cyaniding-vats, the cyanide solution, prepared as above stated, is added, covering the materials. The amount should be about one-third of the weight of the dry matter. This first solution is called "strong solution." Its strength naturally varies with the nature of the mineral, ranging from 0.25–0.80%. In the case of ordinary tailings a 0.30% "strong solution" is used; for acid tailings the strength of the solution varies from 0.25–0.50%. In many works 0.60–0.80% solutions are used.

It should be mentioned that the selective action of cyanogen for gold grows in proportion as the solution is less concentrated; therefore the weaker the solution the less foreign metals does the cyanide dissolve. Therefore, the richer in heavy metals the mineral is the weaker the solution to be employed.

The length of the treatment also varies, from 12–24 hours, according to the nature of the mineral. It is always well to remove a sample of the liquid from time to time in order to make sure of an artificial diffusion. In the case of minerals which require several days' treatment it is best to remove the whole of the solution after 24 hours, and to add a fresh solution. And, in the case of certain concentrates requiring several weeks' treatment, the cyanide solution should be renewed every 2 to 3 days.

When the cyanide process was first used the mineral was kept constantly stirred in the vats, but it was soon found out that if this stirring did increase the yield somewhat, on the other hand the decomposition of the cyanide solution was hastened, besides entailing a considerable expense in motive power. Those are the reasons why this *modus operandi* was abandoned and in its place the percolation system just described adopted.

By taking a sample of the solution and pouring it over zinc strips one can see whether the contact with the strong cyanide solution has been sufficient. If the metal grows dull the lixiviation is incomplete.

When the lixiviation is sufficient the solution is transferred to precipitation-vats by means of the cock and the pipe used in removing strong solutions, then a fresh cyanide solution, called "weak solution," containing only 0.15-0.40% potassium cyanide, is added to the mineral. The object is to carry away the gold remaining from the preceding treatment. Only half as much solution is used as in the first treatment, and the time of contact is only one to two hours. A third washing is made with the "weak solution" and a fourth washing with pure water, which removes the last portions of the charged solution. The "weak solutions" are withdrawn by means of the cock and the tube used for that purpose and transferred to zinc boxes.

At the Robinson works the treatment is somewhat different. The solution which has percolated into the false bottom of the vat is pumped on to the mineral of the same vat. Thus the extraction is more complete, and the amount of cyanide solution to be subjected to the action of zinc being smaller the losses of cyanides are appreciably reduced.

Another modification consists in making the cyanide solution, which has already dissolved some precious metal in the first vat, flow from this first vat into a second, and then into a third, etc. The cyanided solutions thus obtained, containing more gold, give a purer precipitate of gold, and thus the losses in cyanide are likewise decreased.

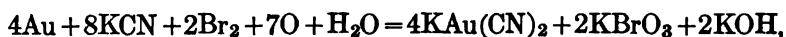
The amount of cyanide of potassium used in practice for the conversion of the gold to the form of gold-cyanide is always much larger than that required theoretically. Theoretically, 718 grams of potassium cyanide are necessary in order to dissolve 1 kg. of metallic gold; but in practice, in order to dissolve 7 grams of gold, contained in 1 ton of tailings, 350 grams of cyanide are required. That is a minimum seldom attained, except in special cases to be studied later; generally 500 grams of cyanide are used per ton of tailings, and sometimes this amount is increased to 700, to 800 grams, and even to 900 grams in certain cases.

De Mesenthal, who had opportunity to study the cyaniding processes in the Transvaal itself, reports that for 1893 the Robinson Company used on an average 625 grams. In 1894 the amount of tailings treated at the Rand amounted to 1,200,000 tons, requiring the use of about 1200 of cyanide, or about 1 kg. of cyanide per ton of tailings.

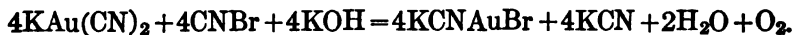
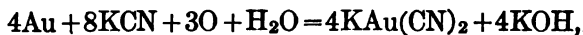
In de Wilde's process very weak cyanide solutions are used by means of a system of circulation and filtration which allows the use of only 105 grams of cyanide per ton of tailings containing 15 grams of gold. Small amounts of caustic soda are added now and then, which facilitates the solution of gold by preventing the action of atmospheric agents, carbonic acid, and water from causing a decomposition of the cyanide. In order to obtain perfect results, de Wilde recommends using red lead; Moldenhauer, using ferrocyanide of potassium; Kendall, sodium peroxid.

Finally, two very similar processes for dissolving gold in potassium cyanide will be mentioned. The results which they produce are quite vigorously disputed, and yet are little known. These methods certainly require a careful study, till now they have been tried only in few cases on a large scale, which fact does not permit of their being judged as to their industrial value. These are Sulman and Mulholland's bromo-cyanide mixed processes.

The first consists in adding cyanogen bromide to the cyanide solution; the second yields the cyanogen bromide during the reaction and consists in simply adding bromine. The reaction may be thus expressed:



or in the case of cyanogen bromide,



As has been already remarked, the halogen acts only indirectly in order to set the necessary oxygen free.

According to Mulholland, bromine displaces the cyanogen of the cyanide, which being set free reacts on gold, forming a cyanide of gold, which is then soluble in potassium cyanide, yielding auro-

cyanide. Mulholland's process therefore consists in forming a gold compound more soluble in potassium cyanide than the metal itself. Bromine should not be in excess, otherwise potassium bromide and free hydrocyanic acid will be formed. In case this happens caustic soda or lime is added. Bromine may be added either all at one time or in small portions; the amount being previously determined according to the percentage of precious metal in the minerals. This process yields 97% of the gold with the use of a smaller quantity of cyanide, and with greater ease and rapidity of solution.

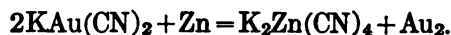
After precipitation with zinc the bromine may then be recovered without appreciable loss.

Such are the chief methods used in carrying on the first part of the treatment of auriferous minerals by the cyanide process. Finally, as has been seen in this rapid review, these methods differ from each other only in the form and size of the apparatus. Nevertheless, the methods have not yet reached perfection. It is evident that the amount of cyanogen consumed is much too large, and the efforts and attention of chemists and manufacturers of gold districts should be centered on this point.

It now remains to take up the second stage of the cyaniding processes—that is the precipitation of gold from the cyanided solutions.

The methods are quite numerous, and will be taken up successively. These processes are of two classes: In the first gold is precipitated by metallic zinc; in the second by electrolysis. There exist other special processes, but they have had but few trials.

**Precipitation of Gold by Means of Zinc.**—The type of these processes is that of MacArthur and Forest. This is based on the fact that zinc displaces gold from its double cyanide as follows:

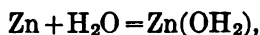


The zinc should have a special shape; as sheets the surface to be acted upon is too small; finely or coarsely granulated, or in powder, gives very unsatisfactory results. The best results are obtained with zinc in the form of shavings freshly prepared.

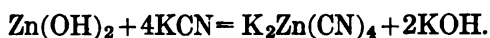
These shavings are so prepared that they present a large surface. Thus 1 kg. of zinc in the form of shavings offers a surface of more than 8 square meters.

Pure zinc is not suitable; only commercial zinc should be used, such as contains some lead, which with the zinc forms a voltaic couple which facilitates the reaction.

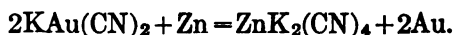
The reaction goes on quite slowly at first, but just as soon as the gold begins to become deposited on the zinc, an electric couple, gold-zinc, is formed which greatly aids the reaction; but, on the other hand, the gold-zinc couple decomposes water by hydrolysis,



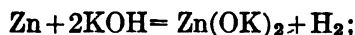
the zinc hydrate dissolving in the excess of potassium cyanide solution,



This is one reason why the amount of zinc used much exceeds that indicated by the general reaction



On the other hand, the alkali produced when the mineral is neutralized, or from the cyanide in which it is always present, and that which is set free by the action of the cyanide, together with that formed in the reaction between zinc hydrate and the excess of cyanide—all this alkali dissolves a fresh quantity of zinc, according to the reaction



potassium zincate acts on the double cyanide of zinc and potassium,



which reaction prevents the liquors from becoming rich in zinc.

In the presence of the excess of cyanide the reaction may be expressed thus:



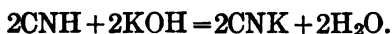
The reaction takes place as above, as the liberation of hydrogen may be noticed in the zinc boxes during the precipitation. Theoretically this hydrogen should have a reducing action on the double



cyanide of gold and potassium, setting gold free, according to the reaction



The reaction does indeed take place thus: Potassium cyanide is formed which is used in dissolving a fresh amount of gold, and metallic gold is precipitated. The hydrocyanic acid set free in the above reaction, coming in contact with the solution itself with an excess of potassa, unites with it in order to form potassium cyanide,



Finally, the liquor should necessarily contain an excess of zinc, which prevents the gold from redissolving in the potassium cyanide. Zinc combined with potassium has a greater affinity for cyanogen than gold combined with potassium has; therefore, when a solution of potassium cyanide is in contact with zinc it will not dissolve the precious metal.

The precipitation of gold, as it is carried on at the works, will now be taken up.

When the solution of potassium aurocyanide is withdrawn from the lixiviation-vats it is conducted into the zinc precipitation-vats, which are arranged in two series. One contains the "strong" solutions, the other the "weak" solutions.

These vats are made of wood, and vary in size according to the works. As a rule, they are 6-8 meters long, 0.6-1.25 meters wide, and 0.7-0.8 meter deep. At the Robinson Company's works they are 6.6×0.6×0.6 meters.

They are slightly inclined lengthwise, and divided into compartments 0.50-0.60 meter long, so arranged that the solution passes from one compartment into another, first from the top, then from the bottom. In these compartments are small boxes or troughs, the bottom of which is a sieve made of iron thread 60 meshes per square decimeter and fixed on a movable wooden frame fastened by beams several centimeters from the bottom of the vat.

In these troughs are placed the zinc shavings (about 18 kg. per compartment). At the head of the box a compartment is left empty in order that the slimes which may come from the lixiviation-vats may be allowed to settle, and likewise at the foot a double

compartment is left empty, which serves to hold back the particles of gold carried away by the following liquid before it comes to the reservoirs.

The charged solutions are allowed to flow through the compartments at such a rate that in 9 hours about 60 tons of aurocyanide solution, representing 225 tons of mineral, are passed through. In this way the loss of gold by being carried away is almost nothing. Gold is precipitated in the form of a blackish powder, which falls through the meshes of the sieve to the bottom of the compartment. The precipitation is generally incomplete if on emerging from the zinc boxes the solution contains more than 3 grams of gold per ton, in which case the operation has been badly conducted; on the other hand, if it does not contain more than 0.7 gram the conditions under which the work is being carried on are excellent.

In the first two compartments the reaction is quite vigorous; almost all of the gold is deposited; zinc is rapidly dissolved and is constantly replaced with shavings from the following compartments so that the last of these is always filled with fresh shavings.

The zinc boxes are emptied twice a month. After adding water in order to remove the charged solution the sieves are withdrawn and shaken so that all the reduced gold which adheres to the meshes may fall to the bottom of the vats. The whole is allowed to stand for 1 hour, and when auriferous slime has been fully precipitated the clear supernatant liquid is siphoned off and transferred to a reservoir.

The walls of the vats are rinsed with pure water, and the mixture of water, gold, and pulverulent zinc is thrown on to a sieve, 16 meshes per square cc. The mixture is stirred with a stick, the end of which is of rubber. In this way the zinc remains on the sieve while the slime containing gold, silver, zinc, lead, tin, antimony, etc., passes through. This slime is allowed to settle in a small vat, placed under the sieve, then dried in shallow pans.

On the other hand, the zinc clippings which remain on the grating are washed and rubbed under water so as to remove as much as possible the gold which adheres to them. The grates are likewise brushed under water. After settling the water is decanted and the mud is added to that of the compartments.

In certain works zinc boxes are used, fitted up with a longitudinal washer situated on the side of the boxes and communicating with each one of the compartments by openings ending below the grating. These openings, closed with a plug during precipitation, are used in allowing the auriferous slime to pass into the washer; the slime falls upon a filter where it is afterwards collected. Generally the zinc boxes are covered with strong iron gratings which may be locked with a key. The auriferous slimes thus collected contain a large amount of zinc and of lead, some silver and copper, traces of antimony, arsenic, nickel, cobalt, aluminum, ferrocyanide of potassium and of zinc, cyanide of potassium and of zinc, cyanide of iron, sulphide of iron, carbonates of potash and lime, iron oxid, silica, etc. These are dried in shallow pans, then they are roasted in order to oxidize the metals and to decompose the cyanides.

This roasting takes place in small muffled furnaces on cast-iron dishes and at a dull-red heat, a temperature which should not be exceeded, the mass being gently stirred so as to avoid any loss of gold dust which is very fine. During this operation carbonic acid and ammonia proceeding from the decomposition of the cyanides are set free. In order to oxidize the zinc more easily it is advised to add 2-3% of potassium nitrate before the roasting. There is thus formed potassium zincate which is less easily reduced than the oxid of zinc.

The roasted mass is then fused in the following way:

An intimate mixture is made of the very dry auriferous precipitate with sodium carbonate or bicarbonate, borax, sand or fluorspar, in the following proportions:

(I) Roasted auriferous slime. ....	820 parts
Carbonate of sodium. ....	85 "
Borax. ....	55 "
Fluorspar. ....	40 "
	<hr/>
	1000 "

Or

(II) Roasted auriferous slime. ....	100 "
Bicarbonate of sodium. ....	50 "
Borax. ....	25 "
Sand. ....	10 "

This mixture is placed in plumbago crucibles which are three quarters filled, and these are placed in a series of three in fusion furnaces. The mass fuses quite rapidly, a very fluid scoria being formed which acts on the crucibles to such an extent that they are soon out of order. As a rule they may be used for no more than six fusions. When the mass has reached the state of quiet fusion the crucibles are removed from the furnaces, and their contents poured into conical-shaped ingot moulds which have been previously rubbed with chalk so as to prevent the slag from adhering.

The metallic portion being heavier falls to the bottom; after cooling the ingots are broken and thus the metallic bottom may be separated from the dross.

The gold thus obtained averages 650 to 800 thousandths; it always contains zinc, lead, copper, and silver in variable amounts. Often the product from many of these operations is again fused with borax at as low a temperature as possible.

Such, in a general way, is the process of MacArthur and Forest. Moreover, it differs from the others only in the method of precipitation, the cyaniding being done practically in the same manner in all the methods. As has been seen, in the precipitation by means of zinc there is formed potassium-zinc-cyanide, which involves an enormous consumption of potassium cyanide. In order to do away with this objection various methods have been proposed, the object being especially to recover the potassium cyanide which is partially lost in MacArthur and Forest's process.

André, chemist of the Deutsche Gold and Silber Scheide Anstalt at Frankfort, proposed the use of aluminum instead of zinc, in which case the reaction is as follows:



As is seen, the cyanide is in this way wholly reproduced, and on the other hand there is formed a precipitate of gold and alumina, the separation of which is rather easy.

That is of an immense advantage, and André's process would certainly be adaptable to trial on a large scale if the cost of aluminium were not so great.

Molloy's process consists in using a sodium amalgam according to the reaction



The charged solution passes through a vat containing mercury, at the surface of which is placed a vertical cylinder containing a solution of sodium carbonate, and dipping slightly in the mercury bath. A sheet of lead dips into this solution. The mercury and the lead thus form two electrodes, united to the two holes of a battery. Under the influence of the electric current sodium is formed,



which unites with mercury, forming an amalgam, which latter decomposes the aurocyanide solution yielding a gold amalgam and a solution of sodium and potassium cyanide better suited to dissolve a fresh amount of gold. Molloy's process is not yet much in use, and the results produced by it are much questioned. However, this process deserves to be kept in mind.

In 1894 Johnstone proposed making the potassium-aurocyanide solution flow on wood charcoal, which is afterward burned in order to extract the precious metal. At present no judgment can be rendered as to the value of this process, which, however, seems to present certain advantages worthy of consideration.

Among the chemical precipitation processes worthy of attention that invented by de Wilde should be cited. It consists of three stages:

- (1) Solution of the gold by means of potassium cyanide.
- (2) Recovery of the excess of potassium cyanide.
- (3) Precipitation of the gold.

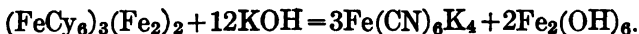
The first operation, or the cyaniding of the mineral, is carried on in the same way as in MacArthur and Forest's process, with this exception (it has already been mentioned in the first part of this chapter), that in this case much weaker solutions of cyanide are used, for it is no longer necessary to use relatively strong solutions in order to avoid the incomplete precipitation by the zinc.

When the gold has been dissolved in the cyanide the recovery

of the excess of cyanide is immediately taken up. To do this ferrous sulphate is added to the solution, small portions at a time, with constant stirring. There is formed a precipitate, which at first is yellowish red but later becomes green, which is a double cyanide of iron and potassium,  $\text{Fe}_2\text{K}(\text{CN})_3$ , the reaction being as follows:



The precipitate is separated by means of a filter-press, and allowed to stand in air, where it becomes rapidly converted into Prussian blue,  $[\text{Fe}(\text{CN})_6]_3(\text{Fe}_2)_2$ ; this Prussian blue is then treated with a strong caustic potash solution, and is converted into iron hydrate and potassium ferrocyanide,



The iron hydrate is filtered, the ferrocyanide filtrate being converted into cyanide by the ordinary methods.

The ferrous sulphate should be added in slight excess, otherwise it would be detrimental. This is controlled by adding a few drops of ferricyanide to the solution, and when this solution is colored blue, enough ferrous sulphate has been added.

Before adding the ferrous sulphate the alkalinity of the solution should be determined. It should be scarcely sufficient to turn litmus paper, for if it be too alkaline the addition of ferrous sulphate will cause a precipitation of ferrous hydrate which would remove part of the gold.

The precipitation of gold by de Wilde's process is based on the fact that if a solution of copper sulphate be added to the potassium aurocyanide solution, acidified with sulphurous acid, the potassium aurocyanide will be decomposed with formation of gold cyanide and copper cyanide, which are precipitated, as in the reaction



The cuprous cyanide results from the action of sulphurous acid on cupric cyanide,  $\text{Cu}(\text{CN})_2$ , which is first formed so that the following is obtained:

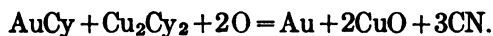


Either sulphurous acid may be used, or an alkaline bisulphite; this is added until a slightly acid reaction is perceptible.

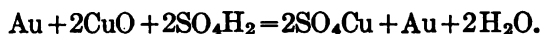
The copper sulphate should be added in slight excess if a complete precipitation is desired. The point of excess may be determined by testing with potassium ferrocyanide, which with a copper salt gives a red precipitate of cupric ferrocyanide.

The operation is carried on in large vats. The whole is allowed to stand for 10–12 hours, then the solution is decanted through the cocks, and the precipitate washed and dried.

It is then ignited in order to convert the aurous cyanide into metallic gold and the cuprous cyanide into copper oxid,



The ignited product is then heated with sulphuric acid 60° B., which dissolves the copper, leaving the gold behind:



The copper sulphate is thus recovered.

De Wilde's process has been applied with success in the Transvaal gold districts by Loevy, and the results obtained have been in all points satisfactory, not only from the standpoint of economy but also from the completeness of the extraction. The following are some of its advantages:

(1) Very much less consumption of potassium cyanide (5 or 6 times less than in MacArthur and Forest's process).

(2) The almost complete recovery of the excess of potassium cyanides.

(3) Likewise the almost complete recovery of the precipitating agent. These advantages the MacArthur process does not possess.

Besides these methods, which are based on purely chemical reactions, are processes based on the use of electricity as a means of precipitating the gold.

To Siemens and Halske of Berlin belong the honor of having applied electrolysis to the extraction of gold from charged solutions.

In 1887 Siemens noticed that the gold anodes used in his electroplating works at Berlin lost in weight when they were left in the

charged solution after the current was cut off. This phenomenon attracted the attention of the celebrated electrometallurgist, who is justly called the pioneer of electrolysis, and he immediately sought to profit by it.

In 1888 the first works for the treatment of auriferous solutions by electrolysis were established at Siebenburgen, and in 1889 other works were set up successively in Hungary, Siberia, and in America. At the present time Siemens and Halske's process is in regular operation at the Worcester mines (in the Rand district) belonging to the Rand Central Ore Reduction Company, Limited. It is carried on in this way:

The gold is dissolved by the aid of strong cyanide solutions 0.06–0.08% and weak cyanide solutions 0.01%, in five large vats having a capacity of 75 cubic meters.

The precipitation takes place in four vats, whose dimensions are  $6 \times 2.4 \times 1.2$  meters. The anodes are iron plates 3 mm. in thickness, 2.1 meters long, and 0.9 meters wide, dipping in the potassium-gold-cyanide solution, and held in a vertical position by means of pieces of wood placed on the bottom and on the lateral walls of the vats. One half of the anode dips to the bottom of the vat, while the other goes down to only 2.5 cm. from the bottom. In this way the vats are divided into a series of compartments between which the liquid flows alternately from down up and from up down. The anodes are covered with cloth so as to prevent short circuiting.

The cathodes are thin lead sheets. They are placed between the anodes and fixed on wooden frames which may be easily raised. The vats are covered with a cover locked with a key, and are opened only to collect the gold.

The electric current is furnished by a Siemens dynamo of 8 volts and 600 amperes; it is 6 volts and 10 amperes per ton of mineral. Above 6 volts the cyanide is much decomposed.

The gold is collected once a month. The vats are opened, and one by one the wooden frames supporting the lead sheets are removed and replaced by new ones. This requires but very little time, which is of great advantage as no interruption of work is necessary. The lead sheets upon which an adhering deposit of gold is formed, amounting from 2–12%, are melted and cupelled.



During the precipitation of gold the iron anodes are attacked by the potassium cyanide, forming potassium ferrocyanide, which, reacting on oxid of iron formed, yields Prussian blue, and this is precipitated on the anode, thanks to a special coating with which this is covered. It is collected and treated as usual in order to convert it again into cyanide.

Siemens and Halske's process fulfils the conditions stated by de Germet in his paper before the Chemical and Metallurgical Society of South Africa, which conditions may thus be reviewed:

(1) The cathodes should be of a metal to which gold sufficiently adheres.

(2) This metal should be capable of being drawn out into thin sheets in order that the weight may be as small as possible.

(3) It should be easy to remove the gold from it.

(4) The cathodes should not be more electropositive than the anodes, so as to avoid the production of reverse currents when the current is shut off.

Siemens and Halske's process has been much criticized, and different inventors have modified it in various ways.

First is Keith's process (1895), in which the lixiviation is carried on with 0.01–0.5% solutions of cyanide, to which has been added double cyanide of mercury and potassium 60–300 grams per ton of solution. Gold, an electropositive element when considered in relation to mercury, decomposes the cyanide of this metal, setting cyanogen and mercury free. The latter unites with gold, forming an amalgam, but under the action of the voltaic couple gold is dissolved and the thin film of mercury also dissolves in the cyanide, in order to reproduce the double cyanide, which may then act indefinitely. In practice, the operation is carried on as follows: On issuing from the lixiviation-vats the liquor passes into wooden boxes containing copper plates used as cathodes and arranged as in Siemens' process. Between these copper plates are placed porous jars containing a solution of ammonium chloride or sulphate, into which iron or zinc rods dip, these used as anodes. Under the action of the current, whose electromotive force is about one volt, mercury is deposited upon the copper plates, and it is upon these amalgamated plates that gold is later deposited. They are

cleaned at regular intervals and without interruption, as in the Siemens process.

Not having yet been tried on an industrial scale it is impossible to judge of the value of this process. Nevertheless its inventor claims as advantages:

- (1) The cyanide is not oxidized into cyanate.
- (2) Mercury facilitates the precipitation of gold.

In Pfluges' process, likewise dating from 1895, the electrode on which the gold is deposited consists of metallic nettings separated about  $1\frac{1}{2}$ –3 mm. and of about one thread per millimeter, presenting therefore a very large surface. The bath around the diaphragms consists of a 5% caustic soda solution, and includes zinc sheets, which with the netting form a sort of Daniell pile. The bath is divided by partitions which make it necessary for the soda solution to circulate in such a manner that the points of contact with the netting are increased. According to the author, the entire efficiency of the process is due to the great extent of surfaces which the metallic nettings offer for the deposit of gold.

Finally, may be mentioned the method of Andréoli in 1897, and which is only a modification of Siemens' process, the used oxidized lead anodes, which, it seems, are entirely resistant. These anodes are obtained by placing sheets of lead into sodium plumbate, washing them, and then plunging them into a solution of potassium cyanide, where, under the action of a strong current they become covered with a thin film of lead peroxide.

The cathodes are of iron, and gold deposits on them in a closely adhering form. When the deposit of the precious metal is deemed sufficient, the cathodes are withdrawn and plunged into melted lead, into which the gold dissolves, and when the gold content of the alloy thus formed is high enough it is cupelled. By the use of oxidized lead anodes the formation of ferric compounds, which complicate electrolysis, is avoided.

The yield and the net cost of these processes vary much according to the works and the nature of the minerals treated.

Nevertheless in the Transvaal it is generally estimated that the MacArthur and Forest process gives an average extraction of 70 to 75%, the net cost of treating one ton of tailings by this method being valued at from 8 to 9 francs.

By Siemens' process, the average extraction is 70%, requiring 113 grams of potassium cyanide per ton of tailings. The total expenses are only 3.75 francs per ton, and even 3.1 francs in some cases.

Among the other uses of potassium cyanide must be mentioned gold and silver electroplating. The objects, burnished and scoured, are placed in a bath containing 1 gram gold chloride or silver cyanide, according as it is gold- or silver-plating, and 10 grams of potassium cyanide dissolved in 450 grams of water. A gold or silver sheet is suspended at the positive electrode; it dissolves just as fast as the gold or silver of the bath is deposited on the objects placed at the negative pole, and thus the bath is kept constantly at the same degree of concentration.

It is also used sometimes in reducing metallic oxides.

It may be used in cleaning silverware which has become yellowish. A good formula for this purpose is the following:

Distilled water. ....	1000 parts
Potassium cyanide. ....	30 "
Hyposulphite of soda. ....	20 "
Ammonia—a sufficient quantity to give a decided alkaline reaction.	

Potassium cyanide was for some time used in photography, for fixing the negatives, on account of its property of dissolving gold and silver. It is now replaced by sodium hyposulphite, which has the great advantage of not being poisonous.

It is used in the preparation of soluble garnet (potassium isopurpurate) with picric acid, and in the preparation of cresylpurpuric acid with trinitrocresylic acid.

It is recommended in medicine for combatting neuralgia and migrains (Trousseau). It is given in 0.50% lotions.

Among the other cyanides sometimes used may be mentioned zinc cyanide, which is used in therapeutics as an antispasmodic; silver cyanide used in silver electroplating, and mercury cyanide recommended as an antisyphilitic.

**Ferrocyanides.**—Potassium ferrocyanide is quite extensively used.

A large portion (50%) of the ferrocyanide produced is used in the manufacture of potassium cyanide. The remainder is used in various ways in the arts and trades. It is used in the preparation of potassium ferrocyanide and of Prussian blue.

It is employed in dyeing, where it is used in coloring blue and in weighting. It is frequently used in dyeing silk black with the aid of logwood and with aniline black. It is also much used in the production of steam colors. Of this Lyon consumes about 300 tons annually.

Ferrocyanide of tin, obtained by double decomposition of a tin salt and potassium ferrocyanide, finds quite extensive use in dyeing, in the production of white discharges as substantive colors, and in the production of certain steam colors added to the blues.

The cementation of certain special steel (springs, tools, etc.), also requires the use of some ferrocyanide. In this respect we must mention the remarkable rôle which the cyanides play in cementation.

In 1850, Caron demonstrated to the Academie des Sciences that the steeling substance in cementation was an alkali cyanide formed by the carbon used, the alkali contained in the ashes of this carbon and atmospheric nitrogen. By a remarkable series of experiments Caron proved that carbon without alkali or without nitrogen could not produce cementation, and that cementation was due to the formation of an alkali cyanide, an hypothesis confirmed by the fact that lime, which does not yield cyanide at the temperature of cementation, does not produce this phenomenon. From this Caron concludes that the most favorable conditions for a good cementation are those which permit the formation of cyanides.

The cement, therefore, probably owes its activity to alkali or alkaline-earth cyanides which are formed during cementation, and if these cyanides are not the sole agents of the cementation they are, at least, the most important. But in all probability (experiment demonstrates this) they do not act because of the nitrogen which they contain, but simply as carriers of carbon. This property which the cyanides possess is due to a certain fixedness which does not permit them to give up their carbon except at the temperature at which cementation takes place.

In certain works cementation is still superficially and rapidly

done by means of wood-charcoal. Réaumur recommended as an excellent cement a mixture of wood-charcoal and sea-salt. Deep cementations are obtained with a mixture of 3 parts charcoal and 1 part barium carbonate (barium cyanide being less volatile allows operating at a higher temperature, and for this purpose it is particularly recommended by Margueritte and Sourdeval and Caron).

Potassium ferrocyanide enters into the composition of a very explosive powder, the so-called white gun-powder, exploding by concussion or ignition. This powder was invented by Augendre, and was made of the following substances:

Prussiate of potash.....	1 part
Chlorate of potash.....	2 parts
Sugar.....	1 part

Pole has improved this powder and gives it the following composition:

Prussiate of potash.....	28 parts
Chlorate of potash.....	49 "
Sugar.....	23 "

Its advantages over ordinary powder are:

(1) It is not hygrometric, and keeps better than ordinary powder.  
 (2) It produces more gas and leaves less residue than black powder, which leaves 68% solid residue, while the white powder leaves only 31%. The gas produced consists of a mixture of nitrogen, carbon monoxide, carbonic acid, and water-vapor. The residue is composed of cyanide and chloride of potassium and a little iron carbide.

(3) Its mechanical effect is a little greater. On the other hand, it has the serious objection of strongly oxidizing iron cannon, and at present it is scarcely used.

Ferrocyanide powder is very sensitive to the electric spark.

Potassium ferrocyanide is still sometimes used in therapeutics as a diuretic. It was formerly used as an antifebril, mixed with urea, but to-day it has fallen into complete disuse.

Finally, potassium ferrocyanide is a very important and much used reagent in all laboratories.

**Ferricyanide.**—Red prussiate of potash is quite frequently utilized in dyeing and in printing, because of its very energetic oxidizing properties.

It is used in the production of aniline black and violet. It converts aniline into Perkins' violet. It is likewise used in the production of steam colors direct from wood (logwood, Lima wood, Pernambuco wood, Brazilian wood); it gives either darker shades or converted print colors, puce, reds, violets. It has the advantage of not attacking the steel doctors, and does not copper the colors as do the copper salts.

The printing of calicoes employs large quantities as discharges. Mixed with a soda or potash solution (Mercer liquor) it is used in producing white patterns on fabrics dyed in indigo blue. Likewise a mixture of nitrate of lead and potassium ferricyanide is a very powerful corroding agent. Finally, it is used in manufacturing special papers for photography and blue-prints.

**Prussian Blue**—This compound, which formerly was utilized to a great extent, is not much used to-day. The discovery of artificial blues has completely dethroned it, and moreover the colors which it gives on fabrics, although they are fixed enough even on contact with acids, are, however, objectionable because they are not resistant to soap, and especially to alkalis.

Coloring with Prussian blue is always obtained by the direct formation of the coloring substance on the fabric, by first fixing ferric hydrate on the fabric and then passing through a potassium ferrocyanide bath acidified with a mineral acid.

Prepared Prussian blue is used in oil-painting, in the bluing and printing of papers and calicoes, and at present is especially used as a plastic color.

**Sulphocyanides.**—Sulphocyanide of potassium as such has no place in the arts and trades. It is especially used in the preparation of sulphocyanides of tin, aluminium, and copper, which are more or less used. Aluminium sulphocyanide is sometimes used instead of the acetate in printing steam reds and pinks. Not being acid as is aluminium acetate, it has the advantage over the latter of not attacking the steel doctors, and moreover of giving clearer and more brilliant reds than those of the acetate. Sometimes sulpho-

cyanide of potassium is mixed with colors in order to avoid attacking the doctors.

Tin sulphocyanide, which is obtained by double decomposition of a commercial tin salt with ammonium sulphocyanide, is quite often used in printing cotton as acid discharges on direct colors.

The canarine, a yellow color which is no longer used, is nothing more than persulphocyanogen, produced by the oxidation of potassium sulphocyanide.

Ammonium sulphocyanide is also sometimes used in photography as a fixing agent.

Mercury sulphocyanide was for some time used in the preparation of a toy known as Pharaoh's serpent and invented by Barnett in 1866. When this salt is mixed with potassium nitrate and lighted, it puffs up and twists and winds about, making it appear like a serpent. This phenomenon is due to an abundant liberation of nitrogen and vapors of carbon bisulphide and mercury. This toy is rather dangerous, as mercury sulphocyanide is a very poisonous compound. Moreover, the same results may be obtained by oxidizing with nitric acid the residue of the purification of brown coal-oils (Vorbringer).

Sulphocyanide of copper is much used in the preparation of submarine paints. The coat applied to the hulls of ships prevents by its toxic properties the crustaceans from adhering to the vessel.

Potassium or ammonium sulphocyanide is frequently used in the laboratories in testing for ferric salts, or for the presence of nitrous compounds in nitric acid.

Among the other cyanide compounds that can be used may also be mentioned calcium cyanate, which a few years ago was highly praised as a fertilizer by Camille Faure, and hydrocyanic acid, sometimes used in medicine in pulmonary diseases, and those in which inflammation is seriously induced, such as asthma, whooping-cough, etc.

## CONCLUSIONS.

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FROM the technical and economic study which has just been made, it follows that the cyanide industry has been improved in a remarkable way, especially in the last fifteen years, and that it is now in a most interesting period of progress.

As we stated at the beginning of this work, the increase in the demand has been the chief cause of these improvements.

At the present time the old processes, i.e., those based on the use of nitrogenous organic substances, are only used in rare cases. Cyanides are now produced almost wholly:

- (1) By new processes, known as synthetic processes.
- (2) By illuminating-gas and the residues produced in its manufacture.

The question naturally occurs to one, Of all these processes belonging to one or the other category, which is or which are the best? This question is very hard to solve. Nevertheless, by relying on the results obtained, it may be possible to a certain degree to answer that question and that is what will now be attempted.

The synthetic processes have the great advantage of producing potassium cyanide as a final product. But in most of these processes this advantage is counterbalanced by serious objections: the temperature required for the reaction is often very high, from which it follows that losses by volatilization occur, besides a rapid wear and tear of the apparatus. Moreover, the conversion is very often incomplete, and the reactions do not always take place as simply as the theory would lead one to expect. Notwithstanding the numerous efforts of investigators and manufacturers, very few of these processes have had any really practical application. Not one



of the synthetic processes using nitrogen and alkali metals has yet given satisfactory results. At one time great hopes were placed on the processes which consisted in making atmospheric nitrogen act on metallic carbides; works had even been established at Frankfurt, but the results never came up to expectations, and according to information, this method of manufacture is now abandoned, or is on the point of being abandoned.

On the other hand, the methods using ammonia appear to give satisfactory results. Among those which still use the oxides or carbonates of the alkalis, two only deserve to be kept in mind: those of Roca and of the Stassfurter Chemische Fabrik. The latter, however, established on a large enough scale, seems to give rather unsatisfactory results.

Only the methods which start with an alkali metal (sodium), carbon, and ammonia, with the intermediary formation of cyanamide, seem to have succeeded. The results obtained by the Deutsche Gold und Silber Scheide Anstalt confirm this statement. The one serious objection is the relatively high cost of metallic sodium or its alloys.

The synthetic processes have been developed especially in Germany and England, and that is the reason that the cyanide industry has become so important in those countries, and that they are able to deliver these products much cheaper than others.

The second class of methods for the production of cyanides, which consists in the extraction of cyanogen compounds from the residues of the manufacture of illuminating-gas or from gas itself, cannot, properly speaking, be considered as a means of manufacture, as it is but an adjunct of the gas industry, on which it depends absolutely. Nevertheless, if gas manufacturers could see what benefits there are to be derived from it, it would constitute a profitable and important source of the cyanide production, and probably might provide for a great portion of the demand. This class of processes may therefore be of great service, especially if one considers that these compounds form themselves, and that without injuring the quality of the gas produced, the manufacturer may still increase the amount of cyanogen compounds; and, finally, that their recovery is made with very little expense.

The processes which extract the cyanogen from the gas directly are those which appear to give the best results, economically as

well as from the standpoint of yield, and among these the processes of Julius Bueb seem to have an important future industrially on account of their simplicity and the very satisfactory results which they furnish.

It is true that the gas industry yields only ferrocyanides which it is then necessary to convert into sodium or potassium cyanide.

As we have seen, this conversion is done very simply by the Rossler-Hasslachner Co.'s process; that is, by means of metallic sodium. This process is practically the only one now in use, and it gives excellent results. When the price of sodium does not exceed 250 francs per 100 kg., this process is profitably conducted, otherwise not. This same statement also applies to synthetic processes using this metal.

Another class of processes very similar to those based on the manufacture of gas is that which consists in converting the nitrogen of the sugar-beet vinasses into cyanides. As is well known, the sugar industry has grown enormously in Germany and France, and it has been seen that the dry distillation of vinasses may profitably produce cyanides. Here again, the discoveries of Bueb of Dessau seem to give the best results; therefore it is to be hoped that soon all the manufacturers, distillers, or gas-makers will know in France, as well as in England and Germany, how to derive all the cyanogen which their industries are capable of producing, and that under the simplest and most profitable economic conditions.

#### DENSITY OF SOME CYANOGEN COMPOUNDS.

Name.	Density.	Weight per Liter.
Cyanogen.....	1.8064	2.335 (0° at and 760 mm.)
“ liquid.....	{ 0.866 at 17°.2	
	{ 0.706 at 7°	
	{ 0.7058 at 7°	
Hydrocyanic acid (anhydrous liquid).....	{ 0.6969 at 18°	1.210 (at 0° and 760 mm.)
Hydrocyanic acid, gas.....	0.947	
Ammonium sulphocyanide. . .	1.31	
	(1.3075 at 13° Clarke)	
Potassium cyanide.....	1.52	
“ ferricyanide. ....	1.83	
“ ferrocyanide.....	1.91	
“ sulphocyanide. . .	1.89	
Sodium nitroprussiate, crystallized.....	1.71	

## TENSION OF CONVERSION OF CYANOGEN.

(L. TROOST AND HAUTEFEUILLE.)

Temperature.	Tension of Conversion.
502. ....	54 mm.
559. ....	123 "
575. ....	129 "
587. ....	157 "
599. ....	275 "
601. ....	318 "
620. ....	868 "
640. ....	1310 "

## HEAT OF FORMATION OF CYANIDES.

Name.	Components.	Heat Liberated, the Compound being			
		Gas.	Liquid.	Solid.	Dissolved.
Potassium cyanide. ....	CN + K	—	—	+ 67.6	64.7
Sodium " .....	CN + Na	—	—	+ 60.4	+ 59.9
Calcium " .....	CN + Ca	—	—	—	+ 57.7
Barium " .....	CN + Ba	—	—	x - 4.3	x - 3.4
Zinc " .....	CN + Zn	—	—	+ 29.3	—
Mercury " .....	CN + Hg	—	—	+ 11.9	+ 17.9
Silver " .....	CN + Ag	—	—	+ 3.6	—

## HEAT OF VOLATILIZATION (FROM LIQUID STATE).

ON BASIS OF ONE VOLUME OF VAPOR (22'.22) = 1 MOL. IN GRAMS.

Hydrocyanic acid. ....	CNH	-5.7
Cyanogen chloride. ....	CNCl	-8.3

## HEAT OF SOLUTION IN WATER IN GASEOUS STATE.

1 MOL. = 22'.22(1 +  $\alpha$ ) AT 760 MM.

Hydrocyanic acid. ....	+6.1
Cyanogen. ....	+6.8

## CRITICAL TEMPERATURE OF CYANOGEN (DEWAR)

Critical tem.	Atmospheric pressure.
124° 0. ....	61 7

## HEAT OF FORMATION OF CYANOGEN COMPOUNDS (BERTHELOT).

Name.	Components.	Compounds.	Mol. Equiva- lent.	Gas.	Liquid.	Solid.	Dissolved.
Cyanogen.....	C <sub>2</sub> diamond + N	C <sub>2</sub> N	26	-37.3	—	—	- 33.9
Hydrocyanic acid.....	C <sub>2</sub> + N <sub>2</sub> + N + H	C <sub>2</sub> NH	52	-74.5	—	—	- 67.9
Cyanogen chloride.....	Cy gas + H	C <sub>2</sub> H	27	-29.5	-23.8	—	- 23.4
Ammonium cyanhydrate.....	C <sub>2</sub> diamond + N + Cl	C <sub>2</sub> NCl	27	+ 7.8	+13.5	—	+ 13.1
Potassium cyanide.....	C <sub>2</sub> diamond + N + H <sub>4</sub>	Cy + Cl	61.5	-35.7	-27.2	—	+ 10.5
Sodium cyanide.....	C <sub>2</sub> diamond + N + H <sub>4</sub>	C <sub>2</sub> NH.NH <sub>3</sub>	44	+ 1.6	+ 9.9	—	—
Mercury cyanide.....	Cy + N + H <sub>4</sub> + K	CyAm	44	—	—	+ 3.2	- 1.2
Potassium cyanate.....	C <sub>2</sub> diamond + N + K	C <sub>2</sub> NK	65.1	—	—	+ 40.5	+ 36.1
Sodium cyanide.....	Cy + K	CyK	65.1	—	—	+ 30.3	+ 27.4
Mercury cyanide.....	Cy + Na	CyNa	49	—	—	+ 67.6	+ 64.7
Potassium cyanate.....	C <sub>2</sub> diamond + N + Hg	C <sub>2</sub> NHg	126	—	—	+ 60.4	+ 59.9
Sulphocyanic acid (Jo).....	Cy + Hg	CyHg	126	—	—	- 25.4	- 26.9
Potassium sulphocyanate (Jo).....	C <sub>2</sub> diamond + N + K + O <sub>2</sub>	CNKO <sub>2</sub>	81.1	—	—	+ 11.9	+ 10.4
Sodium sulphocyanate (Jo).....	CyK + O <sub>2</sub>	CyKO <sub>2</sub>	81.1	—	—	+ 102.0	+ 96.8
Ammonium " (Jo).....	Cy + S <sub>2</sub> + H	CyS <sub>2</sub> H	59	—	—	+ 72.0	+ 69.7
Mercury " (Jo).....	Cy + S <sub>2</sub> + Na	CyS <sub>2</sub> K	97.1	—	—	+ 87.8*	+ 19.9
Hydroferrocyanic acid.....	Cy + S <sub>2</sub> + N + H <sub>4</sub>	CyS <sub>2</sub> Na	72	—	—	—	+ 81.7
Potassium ferrocyanide.....	Cy + S <sub>2</sub> + Hg	CyS <sub>2</sub> Am	72	—	—	+ 59.1	+ 77.1
	3HCy dissolved + FeO ppt.	CyS <sub>2</sub> Hg	158	—	—	+ 18.0	+ 53.4
	Fe + H <sub>2</sub> + 3Cy	Cy <sub>2</sub> FeH <sub>2</sub>	108	—	—	+ 53.4	—
	3HCy dissolved + 2KO dissolved + FeO ppt.	Cy <sub>2</sub> FeH <sub>2</sub>	108	—	—	+ 53.4	+ 53.6
	Fe + K <sub>2</sub> + Cy <sub>2</sub>	Cy <sub>2</sub> FeK <sub>2</sub>	184.2	—	—	—	+ 39.9
		Cy <sub>2</sub> FeK <sub>2</sub>	184.2	—	—	182.6	+ 185.3

## HEAT OF FORMATION, THE PRODUCT BEING:

Name.	Componenta.	Gas.	Liquid.	Solid.	Dissolved.
Cyanogen.....	C diamond + N	-73.9	—	—	- 67.1
Hydrocyanic acid.....	Cy + H	+ 7.8	+13.5	—	+ 13.1
Cyanogen chloride.....	Cy + Cl	- 1.6	+ 9.9	—	—
Cyanogen iodide.....	Cy + I	—	—	+ 6.3	+ 64.7
Potassium cyanide.....	Cy + K	—	—	+ 67.6	+ 59.9
Sodium .....	Cy + Na	—	—	+ 60.4	+ 115.4
Calcium .....	Cy <sub>2</sub> + Ca	—	—	—	+117.4
Strontium .....	Cy <sub>2</sub> + Sr	—	—	—	x-6.8
Barium .....	Cy <sub>2</sub> + Ba	—	—	x-8.6	—
Zinc .....	Cy <sub>2</sub> + Zn	—	—	+ 58.6	—
Cadmium .....	Cy <sub>2</sub> + Cd	—	—	+ 40.0	—
Lead .....	Cy <sub>2</sub> + Pb	—	—	+ 23.6	+ 21.4
Mercury .....	Cy <sub>2</sub> + Hg	—	—	+ 24.4	+ 69.7
Silver .....	Cy <sub>2</sub> + Ag	—	—	+ 3.9	+ 81.7
Potassium cyanate.....	Cy <sub>2</sub> + O	—	—	+ 72.0	+ 77.1
Sulphocyanic acid.....	Cy + H + S	—	—	—	—
Potassium sulphocyanate.....	Cy + K + S	—	—	+ 87.8	—
Sodium .....	Cy + Na + S	—	—	—	—
Mercury .....	Cy <sub>2</sub> + Hg + S <sub>2</sub>	—	—	+ 36.0	—
Lead .....	Cy <sub>2</sub> + Pb + S <sub>2</sub>	—	—	+ 43.6	—
Silver .....	Cy <sub>2</sub> + Ag + S <sub>2</sub>	—	—	+ 16.5	—
Hydroferrocyanic acid.....	Fe + H <sub>4</sub> + Cy <sub>6</sub>	—	—	+ 106.8	+107.2
Potassium ferrocyanide.....	Fe + K <sub>4</sub> + Cy <sub>6</sub>	—	—	+ 365.2	+370.6
Prussian blue.....	Fe <sub>4</sub> + Cy <sub>12</sub>	—	—	+ 556.0	—
Hydroferriecyanic acid.....	Fe <sub>3</sub> + H <sub>5</sub> + Cy <sub>12</sub>	—	—	—	+154.8
Potassium ferriecyanide.....	Fe <sub>3</sub> + K <sub>5</sub> + Cy <sub>12</sub>	—	—	+ 557.4	+528.6
Double cyanide of K and Hg.....	HgCy <sub>2</sub> + 2KCy	—	—	+ 17.6	+ 12.4
" " " K and Ag.....	AgCy + KCy	—	—	+ 11.2	—
Ammonium cyanide.....	CyH + NH <sub>3</sub>	—	—	+ 20.5	—

SOLUBILITY OF CYANOGEN COMPOUNDS IN COLD AND HOT WATER, ALCOHOL, ETC.  
IN 100 PARTS OF SOLVENT.

Name.	Cold Water.	Boiling Water.	Alcohol.	Other Solvents.
Cyanogen.....	4.5	—	23	soluble in ether and es-
Hydrocyanic acid.....	very soluble	—	soluble	sence of turpentine
Potassium cyanide.....	soluble	122	1.2	.
Sodium ".....	soluble	soluble	slightly soluble	
Silver ".....	insoluble	insoluble	insoluble	
Cyanide of silver and potassium.....	12.5	100	4	
Mercury cyanide.....	12	53	56.2	
Nickel ".....	insoluble	insoluble	insoluble	
Gold protocyanide.....	"	"	"	
Protocyanide of gold and potassium.....	14	200	slightly soluble	
Gold percyanide acid.....	quite soluble	quite soluble	quite soluble	
Percyanide of gold and potassium.....	"	"	insoluble	
Platinum cyanide.....	insoluble	insoluble	"	
Magnesium cyanide.....	soluble	soluble	—	
Barium ".....	—	—	—	
Calcium ".....	—	—	—	
Potassium cyanate.....	soluble	soluble	slightly soluble	insoluble in ether
Hydroferrocyanic acid.....	"	"	soluble	
Hydroferrocyanic acid.....	"	"	"	
Sulphocyanic acid.....	"	"	—	
Potassium ferrocyanide.....	soluble in 4 p.	soluble in 2 p.	insoluble	
Sodium ".....	soluble in 4½ p.	—	"	
Ammonium ".....	soluble	soluble	very slightly soluble	
Barium ".....	soluble in 584 p.	soluble in 116 p.	—	
Calcium ".....	soluble in 0.6 p.	—	—	
Ferric ".....	insoluble	insoluble	insoluble	insoluble in weak acids,
Potassium ferricyanide.....	soluble in 3.03 p.	soluble in 1.22 p.	—	oils
Sodium ".....	soluble in 5.3 p.	soluble in 1.25 p.	—	
Potassium sulphocyanide.....	soluble in 1.05 p.	quite soluble	soluble	soluble in tartrate of am-
Ammonium ".....	"	—	—	monia and oxalic acid
Calcium ".....	"	—	—	

## CHARACTERISTICS OF CYANIDES, FERROCYNANIDES, FERRICYANIDES.

	Cyanides.	Ferrocyanides.	Ferricyanides.
Aluminium. ....	—	white precipitate	No precipitate
Antimony. ....	—	white	turbidity due to water
Silver. ....	white curdy precipitate, soluble excess	white	orange, soluble $\text{NH}_4$ , insoluble $\text{HNO}_3$ .
Bismuth. ....	—	white insoluble in $\text{HCl}$	yellow insoluble in $\text{HCl}$
Cadmium. ....	flesh-colored ppt.	white soluble in $\text{HCl}$	yellow soluble in $\text{HCl}$
Cobalt. ....	sulphite of copper + tincture of guaiacum + 1 drop $\text{HCl}$ , blue	yellow-green insol. in $\text{HCl}$	reddish-brown insol. $\text{HCl}$
Copper. ....	white ppt.	reddish brown	yellowish-green ppt.
Stannous. ....	ferro-ferric salt	white, gelatinous, insol. $\text{HCl}$	white soluble $\text{HCl}$
Ferrous. ....	greenish ppt.	white, becoming blue, insol. $\text{HCl}$	blue insoluble $\text{HCl}$
Ferric. ....	—	dark blue	—
Magnesium. ....	—	white conc. solution	brown insoluble $\text{HCl}$
Manganese. ....	—	white soluble $\text{HCl}$	reddish brown, becomes white
Mercurous. ....	—	white gelatinous	—
Mercuric. ....	no ppt.	white becoming blue	—
Molybdenum. ....	apple-green ppt.	brown	yellowish-green, insoluble $\text{HCl}$
Nickel. ....	—	greenish-white, insol. $\text{HCl}$	no ppt.
Lead. ....	—	white	“
Uranious. ....	—	clear brown	“
Uranic. ....	—	reddish brown	yellowish red soluble $\text{HCl}$
Zinc. ....	white ppt.	white gelatinous insol. $\text{HCl}$	no ppt.
Gold. ....	—	emerald green color or ppt.	

## DEGREE BAUMÉ.

WHICH BOILING SALT SOLUTION SHOULD INDICATE SO AS TO PRODUCE BEAUTIFUL CRYSTALS ON COOLING.

Mercury cyanide. . . . .	20° B.
Potassium ferrocyanide. . . . .	38° "
Ammonium sulphocyanide. . . . .	18° "

## COOLING MIXTURE.

A mixture of

Ammonium sulphocyanate. . . . .	133
Water. . . . .	100

produces a lowering in temperature of  $-31^{\circ}$  (Ruddorf).

FORMATION OF DISSOLVED SALTS, DISSOLVED ACID, DILUTE BASE.

FeCy <sub>6</sub> H <sub>4</sub> dissolved +	4KOH. . . . .	+54.0 cal.
	2BaO. . . . .	+56.0 "
	4NH <sub>3</sub> . . . . .	+48.8 "
	$\frac{4}{3}$ Fe <sub>2</sub> O <sub>3</sub> ppt. . . . .	+25.2 "
Fe <sub>2</sub> Cy <sub>12</sub> H <sub>6</sub> dissolved +	6KOH. . . . .	+58.0 "
CySH dissolved +	KOH. . . . .	+14.0 "
	NH <sub>3</sub> . . . . .	+12.5 "

## HEAT OF COMBUSTION.

C <sub>2</sub> +N <sub>2</sub> . . . . .	262.5 cal.
C+N+H. . . . .	158.0 cal. (gas)

## DENSITY OF SOLUTIONS.

## POTASSIUM FERRICYANIDE.

Density.	Per Cent. Potassium Ferricyanide.
1.0261	5
1.0538	10
1.0831	15
1.1139	20
1.1462	25
1.1802	30

## POTASSIUM SULPHOCYANIDE.

Density.	Per Cent. Potassium Sulphocyanide.
1.020	7.0
1.026	10
1.031	11.1
1.034	12.5
1.042	14.2
1.050	16.6
1.070	20
1.077	25
1.137	33.3



## CONCLUSIONS.

## DENSITY OF SOLUTIONS.

## HYDROCYANIC ACID.

Density.	Per Cent. CNH.
0.9988	1
0.9974	2
0.9958	3
0.9940	4
0.9919	5
0.9895	6
0.9869	7
0.9840	8
0.9811	9
0.9781	10
0.9716	12
0.9570	16

## POTASSIUM FERROCYANIDE.

Density.	Per Cent. Potassium Ferrocyanoide.
1.0116	2
1.0234	4
1.0356	6
1.0479	8
1.0605	10
1.0734	12
1.0866	14
1.0999	16
1.1136	18
1.1215	20

## AMMONIUM SULPHOCYANIDE.

Density at 15°.	Per Cent. CNS . NH <sub>4</sub> .
1.020	10.0
1.026	11.1
1.031	12.5
1.034	14.2
1.042	16.6
1.050	20.0
1.070	25.0
1.077	33.0
1.137	50.0

## APPENDIX.

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### DIGEST OF UNITED STATES PATENTS RELATING TO CYANIDE PROCESSES FOR THE RECOVERY OF PRE- CIOUS METALS.\*

THIS digest covers most of the patents included in the following classes and subclasses of the United States Patent Office classification:

Class 75.—Metallurgy.

Subclass 18.—Solutions and Precipitation.

Subclass 86.—Solutions and Precipitation—Apparatus.

Subclass 185.—Cyanides.

Class 204.—Electrolysis.

Subclass 15.—Aqueous Bath, Ores.

Some of the patents in these categories are quite foreign to the subject under consideration, and many but indirectly related to it. It has been thought, however, from the form which discussions of patent issues often take, to include the latter. The aim in making the digest has been to give such a sketch as will indicate the nature of the invention and what is claimed by the inventor, this generally being done by an actual abstract from or paraphrase of the words of the letters patent, but no responsibility is assumed for the opinions, theories, or claims thus set forth. Other related patents may have been granted which do not appear in this digest, because they are not embraced in the subclasses enumerated. Thus, the patents number 229586, to Thomas C. Clark; 236424, to H. W. Faucett; and 244080, to John F. Sanders, do not appear in this digest, because the first two are classified under subclass "Reducing and Separating—Disintegrating Ores," and the third under subclass "Reducing and Separating—Gold and Silver" and neither of these subclasses is included in this digest.

#### CLASS 75.—METALLURGY.

##### SUBCLASS 18.—SOLUTIONS AND PRECIPITATION.

15542—August 12, 1856. W. ZIERVOGEL. *Improvement in processes of separating silver from the ore.*—The application of water or a solution of sulphate of copper slightly impregnated with sulphuric acid instead of lead, quicksilver, or salt, hitherto used for this purpose, to the process of separating silver from copper and other ores, rendering thereby this separation easier, shorter, less expensive, and not noxious to the health of the operator.

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\* Reprinted from "Precious Metals Recovered by Cyanide Processes" by Charles E. Munroe, Ch. D., with the kind permission of the Department of Commerce and Labor.

19991—April 20, 1858. I. GATTMAN. *Improvement in the treatment of sulphureted ores.*—The use of sulphuric acid in connection with the hydrate, carbonate, or sulphate of potash or soda, or with any compound thereof, in the mode of working the native metallic sulphurets.

35842—July 8, 1862. J. SHAW. *Improved apparatus for saving silver from waste solutions.*—Attaching to the waste pipe of the sink or basin into which persons using silver in solutions suffer them to be wasted, a vessel so arranged and constructed that the liquids passing from the sink shall run into, through, and out of said vessel, and between the time of entering said vessel and escaping therefrom shall be brought into contact with such chemicals or metals as will cause the whole or any part of the silver contained in solution to be precipitated and retained in said vessel, while the worthless material is allowed to escape. (This patent was reissued as follows: Reissue 1651, April 5, 1864; reissue 3506, June 15, 1869; reissue 4030, June 14, 1870; reissue 4969, Division A, July 9, 1872; and reissue 4970, Division B, July 9, 1872.)

46875—March 21, 1865. W. BRÜCKNER. *Improved process for refining amalgam.*—The application and use of bichloride of copper, or its equivalent, together with iron pyrites and salt, without reference to the exact proportions of each ingredient.

46983—March 28, 1865. G. W. BAKER. *Improvement in treating ores.*—In order to produce a valuable metal or metals now almost wholly cast away in the treatment of auriferous and argentiferous pyrites, the inventor proposes to take the calcined ores as they come from the furnaces, and, having them well pulverized, subject them to the action of sulphurous acid in tanks located over the main discharge flues of his furnaces, whereby a sufficient heat may be obtained to assist in the reaction of the acid before mentioned. The sulphurous acid thus used is to be formed and collected by compelling the sulphurous vapors discharged from the roasting furnace to pass over, through, and in contact with water, so that sulphurous acid will be formed and collected in a properly arranged tank or tanks, from whence it may be conveyed to the ore tanks, and there mixed with the ore thoroughly by agitation in any manner most convenient. After the ore has been subjected to the action of the acid for a couple of hours the oxide of copper will be replaced by a sulphate soluble in water, and the oxide of iron will be partially brought into the same condition. Should there be any gold or silver held in solution these metals will be reduced to the metallic state. The solution is then drawn off by siphon or otherwise and conveyed to another tank or vat for subsequent treatment, either by cementation or precipitation for the copper and evaporation for the sulphate of iron. The ore thus treated may then be lixiviated by water to wash out all the acid, and this water, which will still hold some dilute solution of the baser metals, may be conveyed to the acid tank and used for the further formation of sulphurous acid. By this means the most concentrated solution is alone permitted to pass to the tank or vat for further treatment. It may be considered a well-settled fact that in all processes of calcination some portion of the precious metals, if such ores are under treatment, escape mechanically or in a vaporized form. This loss, great or small, as the case may be, has heretofore been to a great degree irreclaimable. It is claimed as a part of this improvement that such loss, whether mechanical or in the form of vapor, is wholly prevented by arresting their escape and returning them, either in solution or in the sediment of the liquid acid, to the ore when treated in the ore tanks.

47286—April 18, 1865. W. L. FABER. *Improved process of working silver ores.*—The invention consists in a process which is divided in eight different manipulations, viz., smelting the ore, pulverizing, roasting at low heat, extracting sulphates with water, roasting residue with salt, melting with soda, precipitating silver, precipitating copper.

49637—August 29, 1865. S. F. MACKIE. *Improved process for treating ores.*—The mode of obtaining a rich gold residue from ores of gold by treating the ores by roasting and fusing, and subjecting the roast to the action of acids.

52834—February 27, 1866. J. H. ELWARD and J. L. HAYES. *Improved process for separating gold and silver from ores.*—The process of oxidizing sulphurets con-

taining the precious metals and converting them into sulphates by the use of solutions of nitrates.

**56765—July 31, 1868.** E. LAMM. *Improved method of preparing gold for dentists.*—The use of saccharine substances to precipitate gold from its solutions, thereby forming a mass of crystal shreds extremely useful and convenient for dental and other purposes.

**143368—March 10, 1874.** J. DOUGLAS, JR. *Improvement in extracting silver from its ores.*—The process of utilizing the waste liquors of the ordinary ore-chloridizing process, by allowing the insoluble matters contained in said liquors to precipitate, and then evaporating the clear supernatant liquid to obtain the soluble chlorides, which are reapplied in treating fresh ores.

**207695—September 3, 1878.** J. TUNBRIDGE. *Improvement in separating metals from waste solutions.*—The process of separating precious metals from watery solutions, in which said metals are suspended by passing the watery solutions or suds through a bath of oil or hydrocarbon liquid.

**219961—September 23, 1879.** F. M. LYTE. *Improvement in extracting metals from ores.*—In the treatment of ores containing lead, zinc, silver, and copper, the method of securing the neutralization of the solutions of soluble bases, economizing acid, and carrying over the least possible quantity of silver and lead, which consists in treating the raw ores with an acid solution partially saturated by previous attack on the ores, and treating the partially exhausted ore by raw acid before the latter is admitted to the raw ore, the said steps being conducted in a continuous, alternate, and methodical manner.

**227963—May 25, 1880.** W. M. DAVIS. *Depositing gold from its solutions.*—The process of obtaining gold from its solution by bringing said solution in contact with carbon, and thereby depositing the gold upon it, and of subsequently obtaining the gold from the carbon by calcination or other equivalent means.

**227737—October 30, 1883.** C. A. STETEFELDT. *Process of treating sulphides.*—The process of treating sulphides, such as those obtained from the lixiviation process of silver ores, said process consisting in first exposing said sulphides to the action of dilute sulphuric acid in the presence of nitrate of soda, then converting the nitric oxide which escapes into nitrous acid and nitric acid, and finally carrying on the process by means of a mixture of nitrous acid and nitric acid with dilute sulphuric acid.

**228833—November 20, 1883.** J. MILLER. *Process of recovering metallic particles from water.*—The method of recovering metals in suspension in liquid, consisting, essentially, in forcing such liquid through a filtering medium having a capacity of expansion, and resisted by a rigid inclosing vessel or medium, and then burning the filling material or otherwise separating the metal therefrom.

**290258—December 18, 1883.** J. MILLER. *Apparatus for collecting and saving metallic particles.*—An apparatus for recovering metals or metallic compounds in liquids, consisting of a rigid tank, perforated on one side, in combination with an entrance pipe, provided with a trap and a pressure device.

**290458—December 18, 1883.** J. MILLER. *Method of recovering metals.*—The improved method for recovering metallic particles, slimes, and similar material containing metal from liquids, consisting, essentially, in conducting the liquid and metal-bearing material to a settling tank, allowing the gangue to fall to the bottom, drawing off the liquid, and forcing it under hydrostatic pressure through a filter press, and removing and drying the filtrate.

**292605—January 29, 1884.** C. P. WILLIAMS. *Art of extracting gold by means of alkaline sulphides.*—In the art of extracting gold from ores and artificial gold-bearing products by means of alkaline sulphides, the process, which consists in mixing the gold-bearing material with carbon and an alkaline sulphate (or the equivalents of such carbon and alkaline sulphate), calcining said mixture in a non-oxidizing atmosphere at a temperature below the point of fusion of the charge, cooling the mass out of contact with the air, and leaching the cooled mass with water to dissolve out the soluble sulphides, and recovering the gold therefrom by precipitation.

**377809—February 14, 1888.** T. KIDDIE. *Process of separating precious metals and impurities from solutions of copper, salts, ores, mattes, etc., in acids.*—The process of removing precious metals and impurities from copper mattes, ores, bullion, etc., consisting in dissolving the same after desulphurization and calcination in sulphuric acid, in quantities sufficient to form a neutral solution, and in adding iron hydrates to the neutral solution, whereby the impurities are precipitated and settle with the precious metals not dissolved by the sulphuric acid, leaving a comparatively pure solution of iron and copper salts.

**381809—April 24, 1888.** R. OXLAND and C. OXLAND. *Treatment of ores and materials containing sulphur for the extraction of metals and other constituents.*—The method of treating raw or unburned sulphuret ores of copper and iron to render the copper soluble in water, while leaving the iron for the most part insoluble and rendering the sulphur in the ore available for the manufacture of sulphuric acid, consisting in mixing the finely pulverized ore to a semifluid consistency with sulphuric acid and solution of persulphate of iron, heating the mixture to a temperature such as to evolve sulphurous-acid vapor, and collecting and condensing such acid vapor.

**387688—August 14, 1888.** A. H. LOW. *Extraction of zinc from ores.*—The process of extracting zinc from ores containing precious metals, consisting in leaching the ore with an aqueous solution of sulphurous-acid gas to dissolve out the zinc, and then boiling the leached liquor to expel the sulphurous-acid gas and cause a precipitation of the zinc.

**403615—May 21, 1889.**—E. H. RUSSELL. *Process of leaching ores with hyposulphite solutions.*—The process of extracting metal from ores and metallurgical products, which consists in introducing into the ore or product carbonate of soda, then treating the mass with a solution of sulphate of copper, and then treating it with a hyposulphite solution.

**413808—October 29, 1889.** J. S. MACARTHUR. *Process of leaching ores.*—The process of treating ores containing oxides or carbonates of earth metals, consisting in first subjecting such ores to the action of a proportionate quantity of a solution of a ferrous salt or a bisulphate of an alkali to combine with the oxides or carbonates of earth metals, and then treating the ores with an acid or salt to obtain the contained metals.

**421031—February 11, 1890.** R. PEARCE. *Process of extracting silver from copper ores, mattes, and other copper products.*—The process of separating silver from ores or mattes containing base metals, which consists in mixing with the finely pulverized ore or mattes a quantity of sulphate of sodium or potassium equal to 2 per cent., then roasting the mixture, and finally leaching out by hot water to obtain the sulphate of silver.

**440143—November 11, 1890.** E. DODE. *Process of separating gold and platinum from other metals in solution.*—The process of separating from an acid solution of gold, platinum, copper, and tin the metallic constituents of said solution, which process consists in first subjecting the entire solution in the presence of ether to agitation until the ether becomes yellow, in then decanting the remaining solution from the yellow ether, in then subjecting said remaining solution to agitation in the presence of essence of lavender until the essential oil becomes brown, and in then decanting from the brown essential oil the remaining solution and adding thereto ammonia.

**442016—December 2, 1890.** C. L. COFFIN. *Process of treating ore containing lead, silver, and zinc.*—The process of treating ore containing lead, silver, and zinc to remove the zinc preparatory to smelting, consisting in first roasting the ore, then leaching the ore, filtering the leach fluid through carbon, then subjecting the leach fluid successively to the action of metallic lead and of metallic zinc, and finally precipitating the zinc held in solution in the leaching fluid.

**444997—January 20, 1891.** W. WEST. *Process of treating zinc ores.*—The process of eliminating zinc from complex ores, which consists in roasting the ore to form sulphurous-acid gas and oxidize the zinc, then cooling this gas to a temperature of 180° F. or below, and passing the same in gaseous form in conjunction with steam and without oxidation into sulphuric acid through a previously roasted

charge to form soluble sulphite of zinc, and then immediately leaching out and separating the zinc sulphite with water at a temperature below 180° F.

449814—April 7, 1891. S. W. CRAGG. *Lixiviation process of and apparatus for the extraction of gold or silver.*—The process of restoring the oxygen in a hypo-sulphite solution in the lixiviation process, which consists in passing a current of air through the ore pulp while the said solution is in contact therewith, and a leaching vat, a grating at the top thereof through which ore pulp and water are introduced to the interior of the vat, and a system of crossed separated bars within the vat through which the ore pulp and water pass, combined with an endless-apron filter on which the ore pulp and water fall from the said crossed bars, a trough beneath the filter to receive the water, and a lixiviation vat into which the apron filter discharges the ore pulp.

471616—March 29, 1892. J. LEEDE. *Process of treating refractory ores.*—The continuous process of treating refractory auriferous and argentiferous ores, which consists in subjecting the ore to the continuous action of an oxidizing blowpipe flame in direct contact with the ore at a moderate heat, intermittently subjecting the heated ore to the action of water, agitating the ore, and then repeating the operation at a higher heat, and finally subjecting it to an oxidizing roast without chills, whereby the volatile elements are driven off, the oxidizable elements or compounds are oxidized, and the precious metals are left free and in suitable condition for amalgamation or chlorination.

473186—April 19, 1892. P. C. CHOATE. *Method of producing metallic zinc.*—The process of producing metallic zinc from its ores, which consists in separating the zinc and the equally volatile and more volatile constituents from the less volatile constituents of the ore by the use of heat and a reducing agent, then volatilizing and oxidizing the reduced metal, thereby obtaining a condensed oxidized fume, subjecting this fume to a moderate heat in order to expel its soluble constituents more volatile than zinc, treating the remaining product with dilute sulphuric acid as a solvent, and finally subjecting the resulting solution to the action of an electric current to precipitate the zinc.

481499—August 23, 1892. G. T. LEWIS and C. V. PETRAEUS. *Process of treating sulphide ores of zinc and lead.*—The process of recovering lead and zinc from sulphureted lead and zinc-lead ore, which consists in roasting the ore, then smelting the roasted mass and exposing the fumes or volatile matter produced by said smelting to the action of the gases which are volatilized in the roasting of said ore, together with water, and then separating the zinc solution from the insoluble lead compound and recovering the zinc and lead.

483924—October 4, 1892. T. S. HUNT and J. DOUGLAS. *Process of separating copper from cupriferous nickel ores.*—The method of separating the copper from a solution containing copper oxide and oxides of iron and nickel to produce nickeliferous iron, which consists in first adding common salt to the said solution, then passing a stream of sulphurous-acid gas through the said solution, then precipitating the last traces of the copper in the form of metallic copper, and subsequently crystallizing out the nickel and iron and calcining and smelting the product to obtain nickeliferous iron.

483972—October 4, 1892. C. WHITEHEAD. *Process of treating mixtures containing sulphides of precious metals and copper.*—The process of treating a mixture containing sulphides of the precious metals and of copper, which consists in mixing the sulphides with solution of a salt of silver, whereby a soluble salt of copper is formed and sulphide of silver is precipitated, separating the solution containing the copper from the residue containing the precious metals, roasting this residue to reduce the precious metals to the metallic state, treating the reduced metals with hot sulphuric acid to dissolve the silver, separating the silver solution from the residue, and melting the final residue.

490068—January 17, 1893. F. P. DEWEY. *Process of treating mixtures containing sulphides.*—The process of treating mixtures containing sulphides of silver and copper, which consists in heating the sulphides with strong sulphuric acid to convert the sulphides into sulphates and dissolve the sulphate of silver, adding water, to bring the sulphate of copper also into solution, drawing off the resultant

solution, precipitating the silver therefrom by metallic copper, and recovering the sulphate of copper from the remaining solution.

490193—January 17, 1893. A. FRENCH. *Process of obtaining gold, silver, and copper from ores.*—In processes for obtaining gold, silver, and copper from ores, the treatment of the ores by pulverizing, mixing therewith small percentages of niter cake or bisulphate of soda and common salt, furnacing at a red heat, and then leaching.

497473—May 16, 1893. W. R. INGALLS and F. WYATT. *Process of treating complex or sulphide ores.*—The process of treating complex sulphide ores, which consists, first, in subjecting the ore to a sulphatizing roasting; second, lixiviating the roasted ore with water and sulphuric acid and removing the iron therefrom if necessary; third, precipitating the zinc from said solution in the form of carbonate or carbonate and hydroxide by the use of sodium carbonate and subsequently converting the same into zinc oxide; fourth, evaporating the sodium sulphate obtained from the zinc sulphate solution and heating the same with sodium chloride and coal to convert it into sodium sulphide; fifth, converting the sodium sulphide into bicarbonate of soda by dissolving the same in water and treating the solution with carbonic acid gas; and lastly, converting the bicarbonate of soda into sodium carbonate by heating the same to drive off the hydrogen and carbonic acid gas.

509058—November 21, 1893. E. WALLER and C. A. SNIFFIN. *Method of concentrating ores.*—The method of concentrating argentiferous lead carbonate ores, which consists in dissolving out lead from the ore with the aid of acetic acid real or combined, and water, out of contact with the air whereby the lead and carbonic acid eliminated from the ore are rendered capable of utilization in the arts, and the undissolved silver is concentrated in the residue.

509633—November 23, 1893. D. K. TUTTLE and C. WHITEHEAD. *Process of treating precious metal-bearing slimes.*—The process of treating precious metal-bearing slimes, which consists in subjecting the slimes to the action of dilute acids to dissolve the metals and oxides soluble therein and to the action of a solution of a salt of silver to remove metals more electro-positive than silver that are present in the metallic state.

509634—November 23, 1893. D. K. TUTTLE and C. WHITEHEAD. *Process of refining slimes from the electrolytic refining of copper.* The process of treating slimes from the electrolytic process of refining copper, which consists in removing arsenic, antimony, tellurium, bismuth, and other impurities present as oxides by treating the slimes with dilute acid and heating the purified slimes with strong hydric sulphate.

513490—January 30, 1894. S. H. EMMENS. *Process of treating zinc-lead-sulphide ores.*—The process of treating zinc-lead-sulphide ores carrying gold or silver or gold and silver, which said process consists in, first, finely comminuting the ore; second, roasting the same in an oxidizing atmosphere; thirdly, leaching such roasted ore with water containing ferrous sulphate; fourthly, leaching such once leached ore with an aqueous solution of ferrous and ferric sulphates; fifthly, leaching such twice leached ore with water containing ferrous sulphate; and sixthly, removing iron from the zinc sulphate solution obtained by the first and second of the said leachings by mixing such solutions together and heating them.

516016—March 6, 1894. W. R. INGALLS and F. WYATT. *Treatment of ores of zinc.*—The process of treating ores of zinc, which consists, first, in subjecting the ore to an oxidizing roasting; second, lixiviating the roasted ore with water and sulphuric acid; third, separating one-fourth of the zinc-sulphate solution thereby formed from the rest and precipitating the zinc from said separated portion by means of a sulphide of an alkaline base; fourth, evaporating the remainder of the zinc-sulphate solution to dryness and mixing the precipitated sulphide therewith; and lastly, heating the mixture in a suitable furnace whereby sulphurous anhydride gas is evolved.

518890—April 24, 1894. L. KLOZ. *Process of extracting zinc from ores.*—The process of treating zinc ores, which consists, first, in the preparation of a concentrated solution of sulphurous acid; second, in leaching the ores or furnace products

with this solution to form a concentrated zinc sulphite solution free from sulphates; and third, scattering this solution by steam to dispel the sulphurous acid and precipitate the zinc sulphite.

527473—October 16, 1894. P. ARGALL. *Cyanide and chlorination process for treating gold- or silver-bearing ores.*—In the process of preparing gold- and silver-bearing ores for the extraction of the precious metals, the improvement consisting in separating the slime from the granulated ore, preventing the forming of acid in the slime by mixing lime therewith, and then forming the mixture into lumps for burning.

541374—June 18, 1895. E. B. MIERISCH. *Process of extracting gold and silver from their ores.*—The process of extracting gold and silver from oxidated or roasted ores, which consists in mixing the ground ores with sodium hydrate, mixed with a corresponding quantity of calcium hydrate, then subjecting the mixture to the action of chlorine, whereby the ores are acted upon by chlorates, and hydrochlorites formed "in statu nascendi," and then leaching the lye with a concentrated sodium-chloride solution, the deterioration of which is prevented by the addition of the calcium hydrate to the sodium hydrate.

541447—June 18, 1895. H. F. WATTS and A. COAN. *Process of reducing zinc slimes.*—The process of treating zinc slimes containing the precious metals, which consists in first treating the same with dilute sulphuric acid for the purpose of removing metallic zinc, washing the residue to remove the soluble salts and the remaining acid, and boiling the residue thus formed with concentrated sulphuric acid to dissolve the cyanide of zinc and the other salts thereof which are insoluble in the dilute acid.

541659—June 25, 1895. J. J. CROOKE. *Process of and apparatus for extracting silver from its ores.*—The process of extracting silver from its ores, which consists in roasting the ores with chloride of sodium, treating the roasted mass with a hot aqueous solution containing chloride of sodium, nitrate of copper, and sulphuric acid, and recovering the silver from the solution.

544499—August 13, 1895. H. BREWER. *Process of utilizing waste lye.*—The process of treating zinciferous or cupriferous lyes resulting from the lixiviation of chlorinated roasted ores, which consists in chemically extracting the metals in the lye, except the zinc, removing the sodium chloride by concentration of the lye, extracting the zinc and chlorine from the remaining lye electrolytically, and effecting the chemical extraction in such manner that the final lye will consist essentially of a solution of calcium chloride.

544612—August 13, 1895. A. CROSSLEY. *Process of manufacturing zinc.*—The process for the manufacture of zinc oxide, which consists in adding sulphuric acid to the metallic ores or compounds, heating the mixture and converting the lead present to an insoluble salt, and depositing any silver or gold present, then diluting with water and converting the other metals present to soluble salts, filtering off the clear liquor, then treating the clear acid liquor filtered off with an alkaline sulphide, precipitating the copper as copper sulphide, then filtering the liquor from the precipitate, treating with an alkali until neutral, passing chlorine into it until all manganese and iron present form manganic and ferric oxides, which are thrown down by a slight excess of alkali, adding an excess of alkali to bring the zinc oxide into solution, and then precipitating the zinc oxide, and filtering off the liquor therefrom.

547587—October 8, 1895. C. V. PETRAEUS. *Method of extracting zinc from complex ores.*—The method of separating zinc from complex ores where it is found as a sulphate or sulphite, which consists in crushing the ore, roasting it, dissolving out the soluble zinc salts in water, adding a solution of sulphuric acid to dissolve out any zinc oxide, introducing live steam to the mixture of ore and solvents to thoroughly mix and heat them, separating the solution of sulphate of zinc from the insoluble parts of the ore, adding chloride of calcium to the solution to convert the zinc into a chloride, separating the solution of zinc chloride from the precipitated calcium sulphate and finally adding quicklime to the solution of zinc chloride to precipitate the zinc as zinc oxide.

556690—March 17, 1896. G. O. PEARCE. *Process of extracting gold from solutions.*—The process of recovering gold and platinum metals from aqueous



solutions of these metals, which consists in passing said solutions through a mass of vegetable carbon having associated with it sulphate of iron, oxalic acid, and tartaric acid.

559614—May 5, 1896. G. A. SCHROTER. *Extraction of precious metals.*—The process of extracting precious metals, particularly silver, from ores and metallurgical products, which consists in leaching the crushed and chloridized ore with a concentrated solution of brine to which has been added a small per cent (one-half to 4 per cent. approximately) of a soluble salt of copper.

561544—June 2, 1896. F. P. DEWEY. *Process of treating sulphides.*—The process of treating mixtures containing sulphides of silver and copper, which consists in heating the mixture with strong sulphuric acid, adding water, adding more mixed sulphides, separating the solution of sulphate of copper from the residue containing the sulphide of silver, and heating the sulphide of silver with strong sulphuric acid to convert it into sulphate.

561671—June 9, 1896. F. P. DEWEY. *Process of treating mixtures containing sulphides.*—The process of treating mixtures containing sulphides of silver and copper, which consists in heating them to a temperature at which the sulphur is oxidized, in an excess of sulphuric acid sufficient to convert the sulphides of silver and copper into sulphates, and bring the sulphate of silver into solution outside of the mass of material treated, thereby oxidizing the sulphur, converting the sulphides into sulphates, and bringing the sulphate of silver into solution in the acid outside of the mass of material acted upon.

571369—November 17, 1896. B. HUNT. *Process of refining gold and silver bullion.*—The process of refining bullion slimes by first roasting the slimes to decompose all cyanogen compounds and carbonaceous matters and then treating the roasted slimes with nitric acid.

586159—July 13, 1897. H. BREWER. *Process of treating zinc sulphide ores.*—In a process of treating zinciferous sulphate lyes resulting from the 'lixivation of chlorinated roasted zinc sulphide ores, adding sodium chloride to such lye to saturation or in excess, and crystallizing out the resulting sodium sulphate (Glauber salt) by refrigeration as a by-product.

587123—July 27, 1897. E. F. TURNER. *Process of treating argentiferous sulphide ores.*—In a process for the extraction of the metal of compound sulphide ores, disintegrating and decomposing the latter by the combined action of aqueous and gaseous hydrochloric acid, neutralizing the acid gases evolved whereby sulphureted hydrogen is obtained, heating the disintegrated ore by means of such sulphureted hydrogen, collecting the sulphur dioxide resulting from the combustion, bringing this gas into contact with sodium chloride in presence of heat, whereby hydrochloric acid gas and sodium sulphate are obtained, and utilizing the former in the process of disintegration.

588476—August 17, 1897. H. A. RHODES. *Process of separating gold and silver or other precious metals from their ores.*—In chemical processes for the separation of gold or other precious metals from their ores, slimes, or compounds, the method of preparing the ores by adding thereto a self-hardening, binding material and forming a porous and rigid mass of the compound whereby the precious metals contained therein are freely acted upon by the solvent.

589959—September 14, 1897. J. J. CROOKE. *Process of treating copper sulphides.*—The process of recovering silver or gold and extracting copper in a metallic condition from copper sulphides associated with iron sulphides, which consists in roasting the pulverized sulphides with sodium chloride at a low heat, leaching the roasted mass with a solution whereby the iron sulphides are largely converted into oxides and the silver and gold are dissolved by and removed with the solution, recovering the silver and gold from the solution, roasting the residuum or tailings, fluxing the roasted tailings with silica and pulverized carbon, gradually melting the roasted and fluxed charge to convert the oxide of iron into metallic iron and desulphurize the copper sulphides to liberate metallic copper and form an iron silicate slag, removing the slag from the melted copper, adding a small per centum of silica to convert any remaining iron oxide or metallic iron into an iron silicate slag, and removing this slag from the copper.

602295—April 12, 1898. E. A. ASHCROFT. *Treating solutions or ores containing zinc for recovering zinc as oxides.*—The process of treating neutral zinc solutions for the production of zinc oxide, which consists in first converting the neutral zinc salt into basic zinc salt by the addition of zinc oxide and then intimately mixing with said basic zinc salt, carbon in approximately the proportion of one-twentieth of the weight of the zinc to be recovered, and heating the mixture to a temperature approximately the melting-point of aluminum.

623154—April 18, 1899. H. HOWARD. *Extraction of zinc and copper from ores.*—The process of extracting zinc and copper from ore or residue, which consists in treating the same with aqua ammonia and ammonium sulphate; separating the copper from the resulting solution; adding sufficient soda to combine with all of the sulphuric oxide present and form sulphate of soda, and evaporating the solution to drive off ammonia, the latter being collected in water; and treating the residue with water to dissolve out the sulphate of soda, the zinc oxide remaining.

624000—May 2, 1899. J. DURIE. *Method of reducing metallic sulphides.*—In the process of causing the solution of metallic sulphides containing lead, subjecting the sulphide ore to a solution of sulphuric acid and a nitrate of an alkali metal at a temperature of about 212° Fahrenheit, washing and filtering the lead sulphate obtained therefrom, dissolving the said sulphate, precipitating by carbon dioxide, washing, and drying the precipitated hydrated carbonate of lead, and recovering the sulphur.

625433—May 23, 1899. M. BODY. *Process of treating sulphureted ores.*—In the process of treating sulphureted ores of a complex nature, comminuting and melting the ore in presence of an alkaline salt and carbon, whereby alkaline polysulphides soluble in water are formed, plunging the melted mass into water, whereby a magnetic precipitate is formed and the polysulphides dissolved in the water, separating the solution from the precipitate, subjecting the same to the action of air and sulphurous-acid gas forced thereinto, whereby monosulphides of iron, together with the precious metals, are precipitated, maintaining the alkalinity of the solution during the operation of precipitation by addition of an alkaline substance, as lime, separating the solution from the monosulphide-of-iron precipitate, extracting from the latter the copper and then the precious metal, and separating the arsenic and antimony from the solution by precipitation.

627024—June 13, 1899. R. THRELFALL. *Method of treating flue dust and fume obtained from sulphide ores.*—In the treatment of flue dust and fume from sulphide ores, the separation of the zinc from the lead constituents by leaching out the former by means of a solution of alkali metal hydrogen sulphate.

630951—August 15, 1899. L. VANINO. *Wet process of extracting silver from its haloid salts.*—The wet process of extracting silver from its insoluble haloid salts, which consists in mixing said haloid salts with a watering solution of alkaline agents, and adding formic aldehyde in the cold.

635056—October 17, 1899. D. O'KEEFE. *Process of treating ore.*—The process of treating ore, consisting of roasting the same while being agitated, for the purpose of mechanical disintegration, subjecting the ore to hydrogen gas under pressure, afterwards to chlorine gas, and then leaching the same with hot salt water.

635695—October 24, 1899. C. MARTIN. *Process of chemically preparing and treating rebellious ores.*—The process of effecting the separation of gold, silver, tin, lead, and platinum, in pulverized rebellious ore containing arsenic and antimony, which consists in effecting sulphurization and disintegration of the said ore, producing a sulphide solution of the metals in said ore, and thereupon precipitating the dissolved metallic compounds other than arsenic and antimony by mingling the same with an oxide of an alkali earth metal.

635793—October 31, 1899. F. W. MARTINO and F. STUBBS. *Process of treating ores containing precious metals.*—The treatment of ores or tailings containing the precious metals by finely dividing the ore, mixing it with calcium carbide, and moistening the mixture with water.

644770—March 6, 1900. R. W. KENNEDY. *Solvent for leaching ores.*—A solvent for leaching ores, comprising sodium thiosulphate, ammonium carbonate, copper sulphate, and potassium cyanide in water.

647989—April 24, 1900. T. RYAN, Jr., and N. HUGHES. *Process of extracting zinc from substances containing same.*—The process of extracting zinc from substances containing the same, consisting in subjecting the raw material to the action of a solution of a caustic alkali, precipitating any lead present by galvanic action, securing the removal of organic matters and iron, manganese, and silicon by the addition of caustic lime and bleaching-powder, and finally precipitating the dissolved zinc in the form of zinc oxide or zinc hydroxide by decaustifying the solution by the addition of an acid.

648354—April 24, 1900. C. G. COLLINS. *Process of extracting metals from their ores.*—The process of extracting metals from their ores, consisting in dissolving out or extracting the metal from the powdered ore by means of a solution of ammonium salt in the presence of an alkali base capable of decomposing the ammonium salt, and then precipitating the metal by the addition of a solution of an alkali metal.

652072—June 19, 1900. G. DE BECHI. *Treatment of ore.*—The method of treating complex ores, consisting in subjecting the ore to a chloridizing roasting, condensing the vapors and gases evolved, treating the roasted ore and the acidulated water containing the condensed vapors and gases with calcium chloride to precipitate soluble sulphates and sulphuric acid as insoluble calcium sulphate, then lixiviating the ore with the acidulated water to obtain a solution of zinc and copper salts and fractionally precipitating zinc and copper from the said solution as hydrated oxides by successive additions of lime.

652849—July 3, 1900. S. H. JOHNSON and H. L. SULMAN. *Process of extracting metals from ores or slimes.*—The method of treating pressed slime cakes containing residual water, which consists in displacing the residual water with an equal volume of a solvent solution, mixing the cakes with a further quantity of solvent solution, removing the metal-bearing solvent solution by pressure, displacing the remaining portion of such metal-bearing solution with water and extracting the metal from said metal-bearing solution, whereby all the operations may be performed with an approximately constant volume of the solvent solution.

653414—July 10, 1900. E. FINK. *Process of extracting copper or other metals from tailings or ores of such metals.*—The process of extracting copper and other metals from tailings or ores of such metals, which consists in subjecting the tailings or ore to the action of a solution containing sulphuric acid and to the action of an oxide or oxides of nitrogen in the presence of air or oxygen under pressure, whereby the metal is oxidized and dissolved and the oxide or oxides of nitrogen are converted alternately into a lower and a higher oxide or oxides, and finally separating the solution from the earthy matter of the tailings or ore and separating the metal from the solution.

654804—July 31, 1900. G. RIGG. *Process of obtaining oxide and carbonate of zinc from materials containing zinc.*—The process of producing oxide of zinc and carbonate of zinc from zinciferous material, which consists in leaching the zinciferous material with a solution of ammonia and carbon dioxide wherein the carbon dioxide is in such proportion to the ammonia as to impart to the latter an approximately maximum zinc dissolving capacity.

656497—August 21, 1900. G. DE BECHI. *Process of treating zinc-bearing complex ores for recovery of zinc or other metals therefrom.*—The method of treating complex zinc ores for the recovery therefrom of copper, zinc, and lead, consisting in separately roasting the ore and an alkali chloride in the presence of air and steam, conveying the sulphurous and sulphuric vapors thus derived from the ore over and in contact with the said chloride during the roasting to obtain hydrochloric acid fumes, condensing the acid fumes, lixiviating the roasted ore with the acid liquor thus obtained to produce a solution of metallic chlorides, and successively precipitating the metals of the metallic chlorides as hydrates by successive additions of alkali.

656544—August 21, 1900. H. HIRSCHING. *Process of treating gold and silver ores.*—The process of treating copper ores, which consists in adding the comminuted ore gradually under agitation to an ammoniated solution, and then adding a diluting liquid to the mixture to obtain a highly concentrated copper solution.

657955—September 18, 1900. H. PETERSEN. *Process of enriching metallic sulphides.*—The process of enriching metallic sulphides, which are mixed with carbonates of the alkali earth metals, consisting in dissolving out the carbonates with an aqueous solution of sulphurous acid.

659338—October 9, 1900. C. G. COLLINS. *Process of extracting zinc and copper from their ores.*—The process of treating ores of copper and zinc, which consists in immersing the comminuted ore in a solution containing sodium sulphate and bisulphate (niter cake), removing the depleted ore and extracting the metal therefrom by electrolytic action, adding more comminuted ore to the remaining solution, and repeating the operation.

659339—October 9, 1900. C. G. COLLINS. *Process of extracting copper and zinc from their ores.*—The process of treating ores of copper and zinc containing other metals soluble in any excess of solution which may be employed above that required to dissolve the copper and zinc contained therein, which consists in introducing the comminuted ore into a solution of sodium sulphate containing hydrochloric and sulphuric acid (salt-cake solution) not exceeding 5° Baumé, and subsequently recovering these metals from the solution.

659670—October 16, 1900. C. J. HEAD and R. C. WILD. *Method of treating telluride ores.*—A process for the extraction of tellurium from telluride auriferous ores and the preparation thereby of said ores or the better extraction of the precious metal therefrom, consisting of a lixiviation and digestion of the said ores in a solution containing about 5 per cent. of caustic potash or soda for a lengthened period of two to six hours, the withdrawal of the solution after such digestion from the said ores, and the recovery of the tellurium from the solution.

660013—October 16, 1900. C. J. HEAD and R. C. WILD. *Method of treating telluride ores.*—A process for the extraction of tellurium from telluride auriferous ores and the preparation thereby of said ores for the better extraction of the precious metal therefrom, consisting of a lixiviation and digestion of the said ores in a solution containing about 5 per cent. of carbonate of sodium or potassium for a lengthened period of two to six hours, the withdrawal of the filtrate, and the recovery of the tellurium from the solution.

663759—December 11, 1900. C. HOEFFNER. *Process of producing solutions of zinc chloride.*—The process, which consists in reacting upon an oxide or insoluble salt of zinc in presence of water with sulphurous acid to form soluble zinc bisulphite converting the bisulphite into a monosulphite by suitable reagents, mixing therewith its equivalent of sodium or potassium chloride and exposing the mixture to heat and air in the presence of a contact substance, such as oxide of iron, in order to convert the monosulphite into a sulphate, separating the zinc chloride from the solution and mixing therewith a sufficient quantity of an aqueous solution of sodium chloride to dissolve the zinc chloride and leave the alkali-metal sulphate practically undissolved.

678210—July 9, 1901. J. W. WORSEY. *Process of treating complex ores.*—Process for the treatment of complex sulphide ores, comprising, first, the reduction of the combined sulphur below 15 per cent. by calcination; secondly, finely powdering the calcined ore; thirdly, adding sodium nitrate; fourthly, boiling the mixed ore and nitrate in dilute sulphuric acid; fifthly, roasting the semisolid mass in a closed furnace; sixthly, dissolving out zinc copper and other soluble salts from the said mass by weak sodium-sulphate solution; seventhly, removing any copper from the solution; eighthly, precipitating the zinc and other metals from the solution; and, ninthly, separating the zinc.

679215—July 23, 1901. H. C. BULL. *Method of extracting gold from sea-water.*—The method of extracting gold from sea-water, which consists in mixing with a quantity of sea-water a proportion of milk of lime to react upon the iodide of gold contained in the sea-water to form iodide of calcium and to liberate the gold, then allowing the sludge formed by the reaction to settle, then drawing off the water and then collecting the sludge and treating it to extract the metallic gold therefrom.

683325—September 24, 1901. H. J. PHILLIPS. *Extraction of precious metals from their ores.*—The method of extracting precious metals from refractory sulphide or telluride ores without roasting, which consists in subjecting the ore with-

out roasting and in the form of a powder, under heat and pressure, to the action of alkaline polysulphides in solution of such weakness that same will have a selective action, namely, will dissolve the elements which are combined with the gold, and for which the polysulphides have a greater affinity than for gold, without dissolving the gold itself, which latter is thus dissociated and can then be recovered by any known suitable process for recovering free gold.

684578—October 15, 1901. C. W. MERRILL. *Precipitant for recovering metals from solutions.*—The combination with a metal capable of precipitating other metals from cyanide solutions, if a gritty, inert, non-metallic material, to increase the surface exposed per unit of weight of the precipitating metals.

689835—December 24, 1901. G. H. WATERBURY. *Process of extracting copper from ores.*—The process of precipitating copper in solution, consisting in placing the solution in a tank or receptacle containing pieces of iron small enough to allow the solution to pass readily therethrough, and introducing hot air under pressure into the solution.

692008—January 28, 1902. O. FROLICH, M. HUTH, and A. EDELMANN. *Separating process for ores.*—In the art of separating metals from ores containing iron among a plurality of metals existing therein in a combined form, the process, which consists in heating the ore to a temperature below the decomposition temperature of the sulphate of the metal to be sulphated, but above the decomposing temperature of the sulphate of any other metal existing in the ore, and then passing over it a gas mixture containing sulphur dioxide and oxygen.

693148—February 11, 1902. E. B. PARNELL. *Process of treating ores.*—In the treatment of refractory ores, the process, which consists in subjecting them to the action of chromic acid and then roasting them.

695306—March 11, 1902. M. M. HAFF. *Separation of the constituents of complex sulphide ores.*—The process, which consists in heating mixed sulphides of zinc and lead with sulphate of an alkali metal, treating the resultant mass with a dissolving agent to dissolve the zinc sulphate and alkali-metal sulphate, while leaving the lead sulphate undissolved, and adding barium hydrate to the mixed solution of zinc sulphate and alkali-metal sulphate to precipitate zinc hydrate and barium sulphate.

699326—May 6, 1902. T. A. IRVINE. *Extraction of copper by the wet method.*—A process for the extraction of copper, consisting in the treatment of the ore within a mixed solution of chloride of sodium and sulphuric acid, in which solution there is an excess by weight of the chloride of sodium in respect to the sulphuric acid.

700311—May 20, 1902. F. ELLERHAUSEN. *Treatment of complex and refractory ores.*—The process of treating complex and refractory ores containing lead, silver, and zinc, which consists in smelting the raw ores, churning the fumes and gases with water to condense and mix them with water, settling out the lead, silver, and part of the zinc compounds from the resulting liquor, as a sludge, separating and drying the sludge and fusing the sludge with caustic alkali, thereby precipitating the lead in metallic form.

702047—June 10, 1902. C. G. COLLINS. *Process of rendering metallic sulphides soluble.*—The process of rendering metallic sulphides soluble, consisting in drenching the crushed sulphide ore with aqueous ammonia, draining off the excess of aqueous ammonia, treating the ore thus moistened to an excess of oxygen, leaching the ore, and repeating the operation until the metal is all extracted from the pulp.

702153—June 10, 1902. J. P. VAN DER PLOEG. *Treatment of ores and materials containing antimony.*—The method of extracting antimony from ores, materials, or residues containing it, consisting in finely pulverizing the material, mixing it with a suitable quantity of powdered quicklime, and then mixing with it an adequate quantity of sulphide of an alkali-earth metal and water, so as to form a solution of the lower and most soluble double sulphides as being the best electrolytes, without the use of artificial heat or application of pressure.

702244—June 10, 1902. A. J. POLMETEER. *Precipitant for treatment of copper-water.*—The precipitant for copper-water, containing in solution a sulphide and an excess of alkali.

702582—June 17, 1902. J. W. NEILL and J. H. BURFEIND. *Process of recovering metals from ores.*—The improvement in treating copper or other ores, consisting in agitating a charge of pulp containing the ore by gas from roasting furnaces charged with material suitable for producing sulphurous-acid gas, separating the resultant solution, precipitating the metal from the solution thereby releasing gas and employing the sulphurous-acid gas released by the precipitating process to enrich the gas derived from the furnace and used in leaching a charge of ore.

704640—July 15, 1902. C. HOEFFNER. *Process of extracting copper and nickel from sulphide compounds.*—The process, which consists in oxidizing roasting copper and nickel sulphide ores or mattes, leaching the sulphate of copper formed, converting this into cupric chloride and then into cuprous chloride, dissolving the nickel salts in the residue by said cuprous chloride, precipitating cuprous chloride from the solutions formed and returning the resulting solution containing some cuprous chloride into the cycle of operations.

704641—July 15, 1902. C. HOEFFNER. *Process of extracting zinc or other metals from their ores.*—The process which consists in reacting on a material containing an oxygen compound of metals insoluble in water and whose chlorides are soluble in a solution of alkali metal chloride, with sulphurous acid and an aqueous solution of alkali metal chloride, whereby a solution is formed containing a chloride of a metal.

706302—August 5, 1902. L. B. DARLING. *Means for extracting precious metals from ores.*—In a gold-extracting plant provided with a substantially flat treating floor of non-absorbent material, a series of longitudinally extending channels formed therein, a transverse groove or end launder in direct communication with said channels, fixed screens or strainers covering the top of said channels and launder, side launders or ducts, and valved connections interposed between and uniting the said end and side launders.

707107—August 19, 1902. J. HERMAN. *Process of treating ores.*—The process which consists in roasting sulphide of copper ore at a low heat to form sulphates of the copper and some of the iron present, and produce a large percentage of ferrous sulphate, leaching the roasted ore, precipitating the metallic copper, and adding salt to the leaching solution before or after the precipitation of the metallic copper, whereby the ferrous salts in the solution are converted to the chloride, and a solution having an excess of salt is produced, and the said solution is adapted to dissolve copper and silver out of carbonate and oxide ores.

707506—August 19, 1902. E. FERRARIS. *Method of treating mixed sulphide ores.*—The process of decomposing mixed sulphide ores by means of concentrated sulphuric acid without the aid of extraneous heat.

709037—September 16, 1902. W. PETHYBRIDGE. *Treatment of telluride gold ores.*—In the decomposition of ores containing telluride of gold, the process of reducing the ore to a finely divided state and then exposing the ore to the action of a solution of ferric chloride alone to attack the tellurium.

715023—December 2, 1902. J. C. CLANCY and L. W. MARSLAND. *Process of treating zinc sulphide ores.*—In extracting metals from zinciferous sulphide ores, roasting pulverized ores with the addition or admixture of lead sulphate obtained from a source external to the ore being treated in quantity proportional to the quantity of zinc the ore contains.

715771—December 16, 1902. F. ELLERHAUSEN and R. W. WESTERN. *Treatment of zinc ores.*—The process for the treatment of zinc ores and other zinciferous matter, consisting in calcining where necessary, wetting with a dilute solution of ammonium sulphate, adding sulphuric acid, washing with ammonium sulphate, and precipitating with aqueous ammonia and heating the precipitate.

715804—December 16, 1902. H. E. HOWARD and G. HADLEY. *Treatment of spent acid from galvanizing works.*—The treatment of spent acid from galvanizing works by adding zinc thereto, separating the solution from the precipitate, treat-

ing with bleaching powder to transform the ferrous salts into ferric salts, then adding alkali to precipitate the iron present as ferric hydrate, and subsequently more alkali for the precipitation of the zinc salts.

716847—December 23, 1902. F. W. MARTINO. *Treatment of ores containing precious metals.*—The process of separating gold from ores containing tellurium, selenium, sulphur, arsenic, antimony, tin, phosphorus, or the like, consisting in grinding the mixture, heating it with powdered barium sulphocarbide in a reducing (muffle) furnace, dissolving out the soluble sulphides thus formed, treating the solid residue with a gold solvent, and precipitating the gold therefrom by the employment of barium sulphocarbide.

717299—December 30, 1902. G. C. STONE. *Extraction of zinc and lead from sulphide ores.*—The method of separating zinc and lead from sulphide ores, which consists in smelting the sulphides, oxidizing the volatile constituents at their exit from the smelting furnace, cooling the resulting fumes and products of combustion to a temperature not exceeding 180° F., and passing them into contact with a solvent which will dissolve out one of the metals and not the other.

717565—January 6, 1903. A. VON GERNET. *Process of extracting copper from its ores.*—The process of extracting copper from its ore, which consists in slowly passing the ore in the form of pulp through a current of sulphurous acid, passed in a direction opposite to that of the travel of the pulp.

717864—January 6, 1903. J. T. JONES. *Method of treating ores.*—The process of mixing with ore, to be treated, a leaching fluid, which consists in confining the mass of ore in a vessel with a body of leaching fluid of lesser specific gravity superimposed upon it, carrying portions of the ore upward in said vessel and releasing it above the body of leaching fluid, to precipitate it through said body and simultaneously convey portions of the leaching fluid below the surface of the mass of ore and releasing it and permitting it to rise through the same.

718099—January 13, 1903. S. C. C. CURRIE. *Method of reducing ores.*—The step in the art of treating pulverized ores containing precious metals, which consists in subjecting the ore, in a closed vessel, to the action of hot air at a temperature which reduces some of the salts in the ore from an insoluble to a soluble condition in water, then washing away the soluble salts with water and then repeating the step with air at a higher temperature.

719132—January 27, 1903. W. PAYNE, J. H. GILLIES, and A. GONDOLF. *Process of treating copper ores.*—The process of treating copper ores, consisting in first roasting to an oxide, next saturating the same with a solution of ferrous sulphate or sulphate and chloride, next roasting again and meanwhile adding a small percentage of iron sulphide or sulphur, according to the percentage of copper present, and finally leaching the hot ore.

719757—February 3, 1903. S. C. C. CURRIE. *Process of treating ores containing precious metals.*—The method of treating ore, which consists in heating the raw pulverized ore in contact with steam, and plunging the heated ore into an aqueous alkaline solution.

723787—March 24, 1903. S. TRIVICK. *Process of extracting metals from ores.*—A process for evolving nascent chlorine and effecting the chlorination of metallic substances in order that they may be extracted from a metalliferous mass by rendering them solvent, consisting in adding to the mass a mixture in definite proportions of two substances, one being dry chloride of lime and the other ferric sulphate, the proportions being such as to result in the formation of ferric hypochlorite and ferric chloride which will evolve nascent chlorine.

723949—March 31, 1903. G. D. VAN ARSDALE. *Process of separating copper from ores.*—The process of extracting copper from ores, or products containing copper, which consists in separating copper from cupric-sulphate solutions, with or without ferrous or other suitable sulphate, and of simultaneously producing free sulphuric acid, by adding to such solutions sulphur dioxide and heating with or without pressure, whereby copper or copper compounds are thrown down in the solid form to be subsequently treated, and free sulphuric acid is formed, and of adding the acid liquors thus obtained, after separation from the copper precipitate, to copper ores, whereby the copper contained in them is dissolved and

the original solution regenerated and the process repeated and thus made continuous.

**724414—March 31, 1903.** G. H. WATERBURY. *Copper leaching process.*—The copper leaching process, consisting in placing the suitably pulverized ore in a leaching-tank, adding water, acid, common salt, and oxide of manganese in suitable quantities, heating the mass by the introduction of steam to a suitable temperature, and finally subjecting the pulp to agitation during a suitable period.

**725257—April 14, 1903.** T. B. JOSEPH. *Gold extraction process.*—The process of extracting precious metals from ore containing the same, when in a suitable condition, which consists in subjecting the said ore to a leaching action of a solution of water, cyanide of potassium, hydrate of calcium, carbon dioxide, and bromine, and subsequently precipitating the precious metals from the solution.

**725548—April 14, 1903.** H. R. ELLIS. *Process of extracting copper from carbonate and oxide ores.*—The process of extracting and recovering copper from its carbonate or oxide ores or from material carrying carbonates or oxides of copper, which consists in subjecting the ore or other material in a crushed or powdered state to the action of a carbonate of soda or its described equivalents until the copper is dissolved and subsequently subjecting the charged solution to electrolytic action.

**726802—April 28, 1903.** B. T. NICHOLS. *Ore-treating process.*—The process for treating ore preparatory to leaching, consisting first in mixing the suitably pulverized ore with lime; second, applying water to the mixture and introducing steam whereby the pulp is agitated and kept at a suitable temperature until certain impurities which retard leaching are freed; third, washing the pulp by the introduction of water and continued agitation; fourth, draining off the water as far as practicable; and, finally, drying the ore.

**729760—June 2, 1903.** G. V. GUSMAN. *Process of reducing and separating silver.*—The process of extracting and separating silver from its ores, which consists in subjecting roasted ores to the action of a preprovided aqueous solution of cupric chloride and cuprous chloride, passing the resulting solution through granulated metal, and removing and collecting the metallic silver from said metal.

**729819—June 2, 1903.** J. F. WEBB. *Apparatus for use in extracting metals from ores.*—A tank for use in extracting metals by chemical process from their ores, having a filter bottom and means for discharging air within the tank and downwardly upon the said bottom, whereby the said bottom is kept free from clogging and air is supplied to agitate the mass within the tank and supply oxygen thereto.

**734683—July 28, 1903.** J. F. DUKE. *Process of obtaining gold from sea-water.*—The process of obtaining gold from sea-water containing the same, which consists in precipitating the gold by carbonate of calcium.

**735098—August 4, 1903.** C. HOFFNER. *Process of obtaining lead or other metals from ores or mattes.*—The process, which consists in leaching compounds containing lead and iron with a solution of cupric chloride containing a solvent of the chlorides of said metals, supplying oxygen to produce oxychloride of copper whereby the iron is precipitated, and precipitating the lead as a sulphite by means of a sulphite of zinc.

**735512—August 4, 1903.** H. HIRSCHING. *Treatment of ores containing gold, silver, copper, nickel, and zinc.*—The process for extracting gold, silver, copper, nickel, and zinc from substances containing the same, which consists in subjecting said substances to the action of an acid, washing with water the substance thus treated, thereby forming solutions containing compounds of gold and base metals, and then subjecting said solutions to the action of ammonia for the purpose of precipitating the gold and recovering the base metals from the solution separately, and also the ammonia.

**739011—September 15, 1903.** F. LAIST. *Process of treating ores.*—The method of generating hydrogen sulphide and precipitating copper, which consists in subjecting an alkaline-earth sulphide in presence of water to the action of carbon dioxide, thereby generating hydrogen sulphide and precipitating the carbonate of the alkaline-earth metal, conducting said hydrogen sulphide into the presence



of copper in solution, thereby precipitating copper sulphide and forming a solvent liquid, treating copper ores with said solvent liquid, and collecting said alkaline-earth carbonate and reconvertng it into sulphide.

740014—September 29, 1903. J. HERMAN. *Process of treating ores*.—A process of extracting copper from ores, which consists in treating ore containing iron to produce ferrous chloride, utilizing the chloride and free acid to dissolve carbonates and oxides of copper, the free acid being adapted to neutralize interfering substances and to attack the surface of the particles of copper oxide or carbonate, and regenerating the free acid by the electrolytic precipitation of copper.

740372—September 29, 1903. C. ROGERS. *Process of extracting zinc from sulphide ores, etc.*—The process for the extraction and recovery of zinc from zinc containing sulphide ores or tailings, which consists in subjecting the same to a partial sulphatizing roast, discharging the same while hot into water, leaching the same with said water and with dilute sulphuric acid, subjecting the leached ores or tailings to a second sulphatizing roast, re-leaching the same with the lixivium from the former leaching, and repeating said operations until sufficient zinc and sulphur are removed.

740701—October 6, 1903. A. M. G. SEBILLOT. *Treatment of sulphide ores*.—A process for treating ores containing sulphur consisting of sulphating the ore in a closed vessel by the action of sulphuric acid upon the metallic sulphides at a temperature above its boiling-point and simultaneously recovering the sulphuric acid used, calcining the sulphated ore at a temperature of 700° Centigrade to dissociate the sulphate of iron to prevent dissolving of a too great quantity of sulphate of iron in the lixiviating liquors, and then lixiviating the calcined ore.

748662—January 5, 1904. A. M. G. SEBILLOT. *Process of treating copper ores*.—The process for extracting pure metals from mineral ores, consisting in treating the ores with sulphuric acid at the evaporating-point of the latter, without roasting, to form sulphates, condensing the surplus acid fumes, and lixiviating the sulphates in successively deeper baths under constant agitation, in a current flowing in direction opposite to the progress of the ores.

749700—January 12, 1904. P. NAEF. *Process of lixiviating ores*.—The method of lixiviating ores or other pulverulent materials, which consists in passing the ore downward in thinly divided layers through an ascending stream of leaching solution and at the same time passing a current of air or gas repeatedly through the ore layers in numerous divided jets, whereby the ore particles are agitated in the solution, and the same volume of gas acts successively as an agitating medium.

752320—February 16, 1904. J. B. DE ALZUGARAY. *Extraction of metals from complex ores*.—In the treatment of complex ores, such, for instance, as contain copper, lead, silver, and zinc in comparatively large quantities, the process of extracting the said metals selectively, which consists in leaching the ore with a solution composed of a mixture of a chloride of an alkali or earth-alkali metal with a chloride of a metal other than those of the alkali or earth-alkali series and an acid before calcination or roasting whereby the copper is obtained in solution then washing and drying the ore, roasting the partially disintegrated ore at a low temperature, extracting the metals from the roasted ore in form of salts by means of a second and weaker leaching solution having a character consonant with the nature of the salt it is desired to obtain, and recovering the metals in the usual way.

754643—March 15, 1904. K. DANZIGER. *Process of separating iron pyrites from zinc-blende*.—A process for separating iron pyrite from zinc-blende, which consists in exposing the zinc-blende to the action of air moisture and heat, and extracting the ferrous salt which has been formed by the oxidizing action by water.

755871—March 29, 1904. T. A. HELM. *Apparatus for treating ore*.—An apparatus for treating pulverized auriferous ores, comprising a rotatable cylindrical tank, radially depending blades in the tank extending the length thereof, a circular brace-frame disposed between the inner ends of the radial blades, as an air pipe leading into the tank, faucets to draw off a liquid from the tank, and means to rotate the tank.

## CLASS 75.—METALLURGY.

## SUBCLASS 86.—SOLUTION AND PRECIPITATION—APPARATUS.

**108158—October 11, 1870.** W. S. LAIGHTON. *Improvement in apparatus for precipitating gold and silver from solutions.*—The invention consists in combining two vessels—one to receive the solution to be precipitated and the other the precipitant—and connecting them by an automatic apparatus that shall deliver a certain quantity of the precipitant into the other vessel every time it is filled and provide for the discharging of the same, the quantity of the solution that receives the precipitant, measured out, being governed by a hydrometer or hydrometric float, which is used to operate the apparatus.

**213382—March 18, 1879.** C. C. BITNER. *Improvement in apparatus for obtaining metallic copper from its solution.*—The invention relates to a novel apparatus for obtaining metallic copper from its solution; and it consists in the employment of a tank or vat having a horizontal perforated diaphragm, upon which is placed a quantity of iron. This tank is filled with a solution of copper, previously prepared from the roasted ore in the usual manner. Through the top of this tank a steam pipe passes and extends below the diaphragm, so that the solution is heated by this injected steam, and, by the motion which its action gives, the deposition of the copper is hastened. By means of peculiarly arranged slides the steam is admitted above the diaphragm through holes in the steam pipe to assist the process, if desired.

**234073—November 2, 1880.** R. SCHULDER and E. H. RUSSELL. *Ore-leacher.*—The invention consists of a circular frame supporting the filter and moving on a circular track above an inclined circular table; and it consists, further, of three stationary rollers, designed to elevate and depress the filter at certain points as it revolves, of a device for feeding the substance to be leached upon the filter, of a device for applying the leaching solvent, and of a precipitating tank to contain the solution passing through the filter.

**243768—October 25, 1881.** J. F. N. MACAY. *Filter.*—The invention relates to improved apparatus for use in effecting the operations of dissolving solids in liquids and producing chemical reactions, and of filtering or separating liquids from solids in chemical and metallurgical processes, in which a soluble substance or substances, mixed or combined with an insoluble substance or substances, is or are to be dissolved separately or together, wholly or partially, in a given solvent or solvents, and the solution separated by filtration from the undissolved residue.

In effecting the separation of liquid from solid matters by filtration it is of importance to keep the filtering surface from being clogged by the particles of solid matter, and to present a clear and unobstructed filtering surface for effecting the rapid separation of the liquid from the solid matters. In the apparatus of the invention this important condition is realized in a very effective manner, the construction and operation of the apparatus being as follows:

Within a cylinder of wood or other material not chemically acted on by the materials treated or the reagents employed is inclosed an inner cylinder of hard wood, or of hard earthenware or stoneware or other material not chemically acted on by the materials treated or the reagents employed, this inner cylinder being perforated with holes and lined internally or externally, but preferably internally, with asbestos cloth or other suitable filtering material.

Between the inner and outer cylinder there is an annular space, and the inner cylinder is kept in place by longitudinal and circumferential partitions, the former of which divide the annular space into a number of distinct compartments each provided with a draw-off cock for running off the liquid when separated by filtration. This cylinder is capable of being rotated, and is provided with doors or manholes in one of the heads by which the matters to be treated may be introduced and the undissolved residue removed; and the cylinder is also provided with a tubular journal or journals for the introduction of steam, water, air, or other liquids or gases, under pressure or otherwise, which may be blown, forced, or drawn into the annular space for the purpose of keeping the filtering surface

clear and of acting chemically or mechanically upon the contents of the cylinder. I place within the inner cylinder the ore or other matter to be treated (previously ground or otherwise reduced to a pulverulent state), together with the reagents or solvents by which it is to be treated. By imparting rotary motion to the cylinder (the draw-off cocks and manholes being closed) the solid matters are brought into intimate contact with the solvents or reagents, and by forcing steam, water, air, or other liquids or gases into the space between the inner and outer cylinders, and thence through the filtering medium into the inner cylinder, any solid matters that may adhere to the filtering surface are disengaged therefrom, whereby the said surface is kept clear, the solid matters are kept in suspension in the liquid, and chemical action, which the liquid or gaseous reagents may be capable of exerting on the said matters, takes place under the most favorable circumstances as regards the intimate mixture of the reagents with the matters and the large surfaces exposed to their action. The annular space between the inner and outer cylinders being divided into compartments by longitudinal divisions, the liquid which passes through into it is carried round by the rotation of the cylinder and flows back into the inner cylinder, thus helping to keep the filtering surface clear and unobstructed. When the soluble substances are dissolved or chemically acted upon, and it is desired to separate the liquid from the solid matters, the draw-off cocks are opened, and then, by giving a slow rotary motion to the apparatus, the liquid may be decanted off from the bulk of the solid matter and at the same time filtered from any such matters which it may hold in suspension by passing through the filtering medium. By this rotary decanting action a practically clear filtering surface, unobstructed by solid matter, is constantly presented for the liquid to pass through.

251718—January 3, 1888. A. E. JONES. *Apparatus for separating gold from quartz and rock tailings.*—The invention consists in the arrangement and application of a suitable fibrous material in combination with machinery, so that the fibrous material will unite or collect to itself the gold and carry and deposit the same to a place designated, where it may be collected and treated as desired in separating the precious metal from its sand and ore. Any fibrous matter that will form a pulp when mixed with water is used to coat a wire-cloth screen as in paper-making, and then entangle the fine gold in suspension in the water.

301460—July 1, 1884. J. L. RUSSELL. *Slime filter.*—The invention consists of a trough containing at intervals within it a series of double filtering boxes covered with wire gauze and filled with charcoal, sponge, or any known filtering substance, and the claims cover the trough poised over filter sections provided with adjustable partitions, as well as the combination of a sand box, a sluice provided with adjustable partitions, filters composed of frames and wire gauzes, and gutters.

325835—September 8, 1886. H. C. and J. A. HENDERSON. *Apparatus for concentrating ores.*—The apparatus for concentrating ores, consisting of an outer tank, an inner tank provided with fabric ends, and a perforated feed-box having its lower end below the top edge of the tank, a space being left between the sides, ends, and bottom of the tanks whereby, when the water is received by the perforated feed-box, it will pass into the inner tank and slowly filter through the fabric ends thereof and flow over the top edge of the outer tank, the fabric ends preventing the formation of a current and causing the particles of ore to be precipitated.

366103—July 5, 1887. O. HOFMANN. *Process of extracting silver from its ores by lixiviation.*—The invention relates to a certain improvement in the lixiviation process by which the ore, after having been subjected to a chloridizing roasting, is introduced in a series of troughs, first, together with water to dissolve the base-metal chlorides, and, second, together with the solution used in the ordinary lixiviation process to dissolve the silver. The ore and water are introduced either by means of a mixing-box or an agitator, and are allowed to flow in these troughs for some distance, and finally conveyed by them into settling-tanks. The water while running in the troughs dissolves the base-metal chlorides. In the settling-tanks the ore separates quickly from the liquid. The latter is drawn off and conveyed to other tanks for the usual treatment. The ore sediment containing the

silver is now sluiced or charged again in a similar series of troughs with a solution which has the property of dissolving chloride of silver, like hyposulphite of lime or soda, concentrated salt solution, Russell's "extra solution" (a compound of hyposulphite of lime or soda and bluestone), etc. By passing through this second series of troughs the silver chloride dissolves. Ore and solution run into tanks which are provided with filter bottoms and allowed to separate. The tailings settle to the bottom, while the clear solution, now containing the silver, is drawn off and conveyed into the precipitation-tanks for the usual treatment.

370871—October 4, 1887. F. F. HUNT. *Apparatus for agitating solutions in the leaching of metals from their ores.*—The invention relates to an improvement in apparatus for agitating the acid solutions formed in the leaching of copper and other ores; and the object of the same is to provide a form of rotary agitator in which the heavier portions of the charge cannot accumulate at the centre of the apparatus and escape the action of the agitating arms, which will also produce a more perfect agitation of the solutions than has heretofore been possible, and which will be more durable and economical to construct than the forms in present use.

Heretofore the agitators used in leaching works have usually been made with flat bottoms and have been provided with stirring or agitating arms of conical shape at the base, arranged to rotate a slight distance above the bottom. In the invention this arrangement is reversed, and the agitating tank is constructed with a cone of small altitude placed apex upward in the centre of the bottom and covering a considerable portion thereof, and is provided with agitators, the arms of which are provided with concave shoes and are arranged to rotate in close proximity to the cone in the bottom of the tank.

412610—October 8, 1889. J. B. HANNAY. *Apparatus for applying chlorine to the extraction of gold from ores.*—This invention relates to means of extracting from ores precious metals, especially gold, in the form of chloride solution. For this purpose an apparatus is employed which consists of a chlorinating vessel, a set of circulating pumps, a filter-press, and a chlorine pump, or sets of these, with suitable communicating pipes, cocks, and valves for operating in the following manner: Having reduced the ore to a fine powder, it is mixed with water or with chlorinated water to a condition of thin sludge, which can be pumped. Then charge the chlorinating vessel with this sludge and apply the pumps to cause its circulation therein, drawing from the upper part and discharging into the lower part, while chlorine gas is pumped into the vessel, preferably to a pressure considerably above that of the atmosphere. After circulation has gone on for some time, until the metal in the ore is mostly dissolved by the chlorine, the sludge is pumped by the circulating pumps into the filter-press, additional pressure being given, if required, by using the chlorine pump to force air into the upper part of the chlorinating vessel. The liquid issuing from the filter-press containing in solution the metallic chloride is treated in any of the known ways for separating the metal and recovering the chlorine. In some cases the solution discharged from the filter-press may be used in a subsequent operation to form the sludge by its admixture with a fresh quantity of pulverized ore, and this may be done repeatedly, so as to obtain finally a filtered liquor rich in chloride.

As it is advantageous to charge the chlorinating vessel with an excess of chlorine above that which enters into combination with the metals, the inventor prefers to collect such excess before discharging the sludge by blowing in a little steam to warm the sludge and allowing the free chlorine thus liberated to pass either into a gasometer or into another chlorinating vessel; or an exhaust-pump may be employed to draw off the free chlorine.

When metals such as silver are present, having insoluble chlorides, the blocks which are taken from the filter-press, and which contain these chlorides, may be reduced to sludge, as before mentioned, and may be subjected to the same treatment with a suitable solvent instead of the chlorine.

418138—December 24, 1889. J. S. MACARTHUR. *Metallurgical filter.*—A metallurgical filtering apparatus for separating a precious metal from a solution containing said metals, consisting of a series of vessels, each of which has an inlet tube near its bottom, an outlet tube near its top, and a perforated false bottom above the inlet tube, zinc sponges disposed in the several vessels, pipes connecting the inlet

and outlet tubes of the several vessels, and a reservoir for supplying the solution to the first vessel of the series.

**425025—April 8, 1890.** D. DENNES and T. K. ROSE. *Apparatus for leaching ores.*—In a leaching apparatus, a movable table, having a flange or wall projecting from its upper surface to form a receptacle for filtering material, the said receptacle being of less diameter than the upper surface of the table, whereby a packing receiving ledge projects beyond the base of the said wall or flange, combined with the leaching cylinder, the lower end of which is constructed to receive said wall or flange, while the ledge abuts against said lower end of the cylinder.

**442262—December 9, 1890.** S. TRIVICK. *Apparatus for treating ores to obtain precious metals therefrom.*—This invention relates to improvements in apparatus forming a plant for treating roasted ground ores to obtain precious metals therefrom, adapted for use in treating roasted ground ores of precious metals that have been roasted by any known or suitable method.

The apparatus consists, essentially, of a vessel (preferably employing a pair at least of such vessels, so as to change from one to the other of the pair in working) having a porous bottom on which the ground-roasted ores rest; means of supply of leaching liquid controlled by valve; means of drawing off leached liquid, conveyance thereof to, and means of stirring said liquid in a mixing chamber—a filter vessel having a porous floor—and means of pumping the filtered liquid to a reservoir; means of evaporating the leaching liquor to recover the contained salts; also recovering the copper salts for reuse, and means of heating the leaching liquid, and also means of desiccating the product.

The invention also consists in a furnace for roasting ores of precious metals, comprising, among other features, a chamber, coils of piping, a tank, reservoir, a force-pump, a system of heating pipes, leaching reservoir, tanks with porous floors, and a mixing vessel with rotating stirrers therein.

**449813—April 7, 1891.** J. CRAGG. *Apparatus for extracting gold or silver from ores.*—In an apparatus for extracting gold or other metals from their ores in solution, a tower and a mixer, which consists of a trough having pipes to conduct the reagents in liquid solution, which enter the same from different sides and terminate out of alignment about centrally of the trough, combined with a hopper placed over the ends of the said pipes and an overflow plate leading to the said tower.

**456323—July 21, 1891.** P. L. GIBBS. *Ore-leaching machine.*—This invention has reference to ore-leaching machines in which a rotating annular series of ore receptacles pass successively under an ore vat containing the crushed ore in a solution to receive their respective contents or to be otherwise filled, and to discharge the filtrate during their transit into a suitably placed discharging conduit or launder and at a predetermined point in their orbital movement and automatically discharge the residuum.

The objects of this improvement are, first, to provide a suitably suspended vat to receive the ore in a solution, or dry or roasted ore, and adapted by suitable openings in the bottom thereof to optionally discharge said contents; second, to provide a series of leaching-vats to pass successively under said primary vat and respectively receive from the latter a proper quantity of its contents; third, to provide suitable mechanism for supporting and progressing said secondary vats; fourth, to provide a conduit or launder to receive and carry off the filtrate from said leaching or secondary vats; and, fifth, to afford facilities to automatically discharge the residuum from said leaching-vats preparatory to their refilling.

**463120—November 10, 1891.** D. DENNES. *Leaching-vat for separating precious metals from their ores.*—An ore-leaching apparatus consisting of a closed vat or separating vessel having a removable bottom carrying a filter-bed in its upper portion and an auxiliary chamber beneath, provided with a removable bottom and a filter-bed, and a suitable pipe connection between the separating vessel and said auxiliary chamber in its bottom.

**464672—December 8, 1891.** W. D. BOHM. *Apparatus for separating gold and silver from ore.*—The inventor places the powdered or divided ore, or material to be treated for the obtainment of the gold or silver, or both, in a vessel or vat, or vessels or vats, and through it passes the leaching solution, preferably pre-

viously heated. By means of a force-pump, the leaching solution is forced up through the ore and through a filter at the top. The solution and the precious metal which it now contains pass into a vessel in which it is agitated with a precipitating agent. From this last-named vessel the solution is forced up by a force-pump through a vessel having a filtering arrangement, such as a porous diaphragm, at the top, so that the solid matter is retained thereby, the liquid passing off to be heated again and to be restrengthened by the addition of the necessary further quantity of leaching chemicals and passed back to the leaching vat or vats for reuse. The pressure under which the liquids are forced up through the leaching-vat and precipitant vessel should be at least eighteen pounds per square inch. At intervals the solid matter retained by the last-named filter vessel is passed into a filter-press or equivalent apparatus, whereby it is deprived of the greater part of its moisture. The ore which has been leached is then drained of all solution and washed free from the last traces thereof with water, preferably hot, and then can be washed out of the vat or vats with acidulated water, and passed over zinc or alloy of zinc with other suitable metal, so that hydrogen is evolved, which reduces any precious metal still remaining in the ore to the metallic state, or such state that it is taken up when the ore is afterwards passed over mercury—for instance, over amalgamated copper.

496385—April 11, 1893. F. WEBB. *Method of and apparatus for extracting precious metals from their ores.*—The inventor claims, in means for extracting precious metals from their ores, the combination of an outer vessel resting in suitable trunnions for containing the reagent or chemical solution, and having inlet and outlet pipes communicating, respectively, with the top and bottom thereof through said trunnions, a perforated vessel in said outer chamber, and adapted to receive the crushed ore, and provided with a manhole opening extending to the outside of the latter, and means for reciprocating the inner vessel and for rotating the outer vessel on its trunnions, whereby the contents of the inner vessel may be discharged. Also, the method of separating precious metals from their ores, consisting in placing the disintegrated or crushed ore in a closed perforated vessel and causing the latter to reciprocate in the reagent or chemical solution, whereby the latter is enabled to more effectually act upon the ore.

497856—May 23, 1893. C. G. BROWN. *Ore-tank.*—In a tank for leaching or saturating ore, the combination with a false bottom and a piece of textile material laid upon the upper side of said false bottom; of a series of vertically disposed perforated tubes designed and adapted to hold the pieces of ore apart and promote the circulation of the leaching or saturating solution.

525970—September 11, 1894. J. STORER and B. T. LACY. *Method of and apparatus for dissolving, leaching, and filtering.*—The inventor claims the improved method of dissolving, leaching, and filtering, consisting, essentially, in connecting a plurality of closed tanks in series, then introducing an expansible medium upon a body of non-compressible fluid contained in a terminal tank to force the said fluid under pressure into the successive tanks and through the material under treatment until it reaches the final tank, then connecting this last-named tank with the initial tank, and finally introducing pressure in the said final tank to force the fluid therefrom so that it may be returned to said initial tank. And in an apparatus for dissolving, leaching, and filtering, the combination of the tank adapted to contain the material to be treated, a tank adapted to contain a non-compressible fluid and connected with a source of steam, gas, or vapor supply, a valve-controlled pipe from said fluid tank to said material-containing tank, a final tank beyond the material-containing tank, a valve-controlled pipe connecting said material-containing tank with said final tank, whereby the fluid is forced into said final tank, a valve-controlled pipe connecting said final tank with the initial fluid tank, and means for admitting an expansive medium into said final tank to force the fluid therefrom back into the initial tank.

530397—December 4, 1894. N. H. CONE. *Filter-barrel.*—In an apparatus of the class described, the combination with a revolvable cylinder having a hollow trunnion, and a head provided with radiating channels having independent valves of a filter arranged in said cylinder and valves for opening or closing said channels independently of each other.

**536981—April 2, 1895.** T. L. WISWALL and J. B. FRANK. *Receptacle for recovering precious metals from solutions.*—This invention relates to apparatus wherein the recovery of the precious metals from cyanide and other solutions is effected by passing the solutions through a filtering material, by which the precious metals are precipitated. And the inventor claims, in apparatus for the extraction of precious metals from solutions, the precipitating box, having an undulating, sinuous passage from end to end, comprising a series of alternate angular depressions and elevations, provided with a series of retaining pins, attached to the interior of said precipitating box, and extending into the precipitating, filtering material within said passage.

**549177—November 5, 1895.** T. L. WISWALL and J. B. FRANK. *Apparatus for recovery of precious metals from their solutions.*—The inventors claim in apparatus for the recovery of precious metals from their solutions a precipitating box adapted to contain a finely subdivided, metallic, precipitating reagent, divided into a series of compartments by removable perforated partitions, said partitions being provided with adjustable gates, controlling the flow of said solution through the perforations in said partitions for the purposes indicated.

**549622—November 12, 1895.** P. ARGALL. *Apparatus for extraction of precious metals.*—The specifications set forth that in the treatment of ores by the cyanide process to extract their gold and silver contents, it is the usual practice to place the ores in open leaching-tanks and allow the cyanide solution to percolate through the mass and so dissolve and remove the precious metals in solution. This method is on the whole fairly efficient, but it occupies considerable time (forty to eighty hours) and causes a large consumption of cyanide through decomposition, owing to its long contact with the ore and atmosphere. With many classes of ore, however, it is found that agitation of the ore and solution is necessary in order to obtain the best results or largest extraction of precious metals. Particularly is this the case with silver-bearing ores or ores carrying considerable value in silver.

The agitators heretofore in use shorten the time necessary to dissolve the precious metals; but they invariably cause a large consumption of cyanide, due chiefly to the continuous agitation of the solution in open tanks or in partly filled barrels in the presence of an excess of air, while the ore when discharged from the agitators is in such a condition that very often it cannot be leached, or at best but part of the cyanide solution containing the dissolved gold can be separated from the ores. Then again, the agitators now in use are of such small capacity as to add largely to the cost of treating the ores.

This invention relates to a new machine for treating ores by continuous agitation and continuous percolation under pressure or by means of vacuum and either with or without external or additional heat. And the inventor claims a percolator for treating ores by the cyanide process comprising an outer shell capable of being closed, air-tight, hollow trunnions upon which said vessel rotates, concentric tubes extending axially through the vessel, the outer tube being covered by a filtering medium, a passage connecting the annular space between the tubes with one of the hollow trunnions, and a pipe communicating with the chamber surrounding the outer tube. The invention includes other features of a minor or subsidiary character.

**552807—January 7, 1896.** H. G. WILLIAMS. *Method of and apparatus for extracting metals from their ores.*—In an apparatus for the extraction of precious metals from their ores by the wet process, the combination of one or more castings, with screw conveyers and mixers, means for feeding the solid and liquid matters thereto, and a dam placed at the discharge end of the casing for each conveyer, having its surface inclined upon the side next to the conveyer flights or blades, for the purpose of maintaining the admixture of the liquids and solids by preventing the liquid from traveling faster than the solid and still giving passage by reason of its incline to the travel of the solids over the same; and, in the extraction of precious metals from their ores by the wet process, the method of continuously and uninterruptedly precipitating and separating the metals, which consists in simultaneously introducing the precipitating agent and an independent agitating blast of steam into the solution of metal in

direction as described to secure admixture and agitation by a whirling motion and the agglomeration of the precipitated particles of metal, and continuously separating the precipitate by settlement and filtration.

567144—September 8, 1896. S. B. LADD. *Apparatus for leaching ores.*—The object of the present invention is to provide an economical and practical apparatus for the lixiviation of ores, and particularly applicable to cases where a large mass of material has to undergo treatment—as, for example, in the lixiviation of low-grade gold ores by the cyanide process—and where the expense of handling material becomes an important factor with respect to the commercial working of the process. The invention applies, generically, to the lixiviation of comminuted or pulverized material of any character, but it is especially designed for the lixiviation of ores by the cyanide process, for in the treatment of ore pulp or slimes by the cyanide and other like processes a large amount of material, often of a low grade, has to be subjected to the action of an aqueous solution of a cyanide or other solvent, or to the successive action of a series of solutions. The common course of procedure in working the cyanide process on a large scale is to run the ore pulp into large vats and then to cause the proper solutions for leaching out the precious metals to percolate therethrough, for example, first an alkaline solution, when the ore is acid, then a strong solution, then a weaker solution, and finally water to wash the pulp. The vat is then emptied and refilled with fresh ore pulp; also, the solvent process is sometimes worked by agitating the pulp and leaching solution in pans or vessels. Both systems require considerable labor and are intermittent.

Another object of the present invention is to provide means to make the extraction process continuous, so that the ore pulp shall progressively and continuously be associated with the solutions or the washings which may be necessary for thoroughly exhausting the values from the ore. This is accomplished by constructing a leaching-tank, in the form of a long trough, which may be divided by one or more fixed or removable bridges into so many trough sections as are required for the several solutions or washings when one leaching is not sufficient; or by providing a series of tanks or troughs operatively arranged with respect to each other, employing in connection therewith a conveyer for the ore pulp adapted to continuously feed the pulp with a steady movement through the several solutions in an uninterrupted flow through the apparatus to the point of discharge without any intermediate stoppage or handling of the same whereby the lixiviation of the ore is effected.

For the purpose of rendering the operation continuous, provision is made for a constant drawing off of the charged solution or solutions from the leaching troughs and an inflow of fresh solution thereto. In the case of the first cyanide solution the inflow is preferably at the ore-entrance end of the trough or trough section and the current is with the ore, thus catching the fine float gold carried by the fresh pulp; but in the subsequent troughs or trough sections, and also in the first, if preferred, the inflow of the solution (or washing water) is preferably made at the ore-exit end and the outflow of the solution is at the opposite end where fresh ore or pulp is entering the trough or trough section. Thus, in this latter case, the flow of the solution is opposite to that of the ore. The fresh cyanide solution first acts upon pulp which is largely leached out, and as the solution becomes more and more charged with the gold or precious metals it meets pulp that is progressively richer in the metals, and the conditions are therefore favorable for effecting a complete extraction of the precious metals by the solvent. As a preferred form of conveyer, slowly-moving blades transverse to the trough or tank are used. These blades extend across the tank with just enough room at the sides for clearance, and they reach from above the surface of the solution down to and into the ore pulp on the bottom of the tank with openings or notches in or along the lower part of the blades for the underflow of the solution. These blades divide the trough or tank into a number of communicating divisions and form what may be called "traveling partitions," moving slowly through the trough from end to end thereof. The lower edges of these blades are preferably fashioned with rake teeth, and they open up and rake along the layer of ore pulp on the bottom of the tank and effect a slow and progressive movement of the mass



with a constant plowing therethrough and exposure of fresh portions thereof to the action of the solution, while the solution in the tank as the series of blades move forward has to flow back through the notches or openings in the bottom of the traveling blades from each of these divisions formed by the blades, respectively, into the adjacent rear division, and thus there is secured a constant and steady underflow of the solution in close proximity to the agitated pulp. This flow of the solution is in addition to and distinct from the flow due to the constant addition of fresh solvent at one end of the trough and the drawing off of the charged solution at the other end thereof; but it will be seen that the underflow thus effected prevents a mere surface flow of the solution from one end of the trough to the other. On the contrary, as the flow from the respective divisions of the trough is from the bottom and under each traveling partition or blade, the overflow or discharge from the trough at the end is necessarily of the charged portion of the solution. It will be seen that this method of leaching ores places the ore and the solvent under perfect control, which is a very great advantage with respect to the economical leaching of ores. There is an agitation and constant shifting of the pulp in the solution, which very much accelerates the action of the solvent and shortens the time required therefor, and the speed of the conveyor can be regulated so that the pulp will not remain in the tank or tanks any longer than is necessary, and yet long enough for the extraction of all value therefrom. On the other hand, the flow of the solvent through a tank can be gauged so that it will issue from the tank fully charged or charged to the degree most profitable under all the conditions of the case.

576118—February 2, 1897. W. F. HEATHMAN. *Means for extracting gold and silver from sea-water.*—In order to extract said metals, the sea-water or salt lake-water is passed through a filter made of carbon, and the gold and silver held in solution in the sea-water or salt lake-water are freed from the chemical combinations in which they occur in the water. The chlorides and bromides of gold and silver in solution when passing through the carbon filter are decomposed by the reducing power of the carbon, the liberation of chlorine, and the destruction of the bromine combination, with the result that metallic gold and silver are precipitated in the carbon filter and deposited in the pores and upon the surface of the carbon. And the inventor claims a tank mounted on suitable supports and provided in its side with an inwardly opening valve or gate, said tank having a perforated bottom, and a filtering medium arranged on the bottom and comprising alternating layers of coarse and fine carbon, a layer of wire-cloth, and a perforated top covering.

584627—June 15, 1897. J. J. DEEBLE. *Apparatus for extracting gold from auriferous material.*—This invention has been devised in order to provide a machine for use in the extraction of gold from auriferous material by the aid of chemical solvents, in order to insure the particles of auriferous material being brought into intimate contact with the cyanide or other solvent solution. It includes a vat or pan to receive the auriferous material to be treated, having at or about its center a vertical shaft or spindle with one or more agitators or stirrers attached to its lower end. Motion is imparted to this shaft or spindle by bevel gearing or other convenient mechanical contrivances, and means are provided for reversing the rotation and controlling the speed of the agitators, as well as for raising or lowering the agitator shaft or spindle. These means may consist of a screw-threaded lifting rod with correspondingly threaded bevel wheel in gear with a bevel pinion fitted with a crank-handle, whereby it may be rotated in the required direction; or, if preferred, a rack and pinion may be used for the purpose. The inner side of the wall of this vat or pan is provided with a series of projections which produce eddies or swirls in the material under treatment as it is carried round the vat or pan. In order to drain or draw off the gold-bearing solvent from said vat, it is provided with a vertically sliding valve. A waste discharge valve may also be provided in the lower part of the vat or pan for the purpose of enabling the waste material to be sluiced therefrom after the gold has been dissolved and the gold-bearing solution has been drawn off through the valve above referred to.

587408—August 3, 1897. H. L. SULMAN. *Method of recovering precious metals from their solutions.*—This invention has for its object the recovery of precious

metals from solutions of the same by means of a new and improved apparatus, the apparatus being constructed to effect the deposition or "precipitation" of the precious metal or metals in solution upon a "precipitating" substance or "precipitant" which is in a solid but more or less finely divided state.

The apparatus is designed to recover these metals from solutions of their haloids by means of the employment therein of dense but more or less finely divided carbon, subsulphide of copper, or other suitable precipitant; again, also, for the recovery of the same metals from their cyanide solutions by means of the finely divided zinc product commercially known as "zinc fume," and generally for analogous requirements.

It is necessary that whatever the nature of the precipitant used and the degree of fineness to which it is found desirable to reduce it primarily, it shall be of greater specific gravity than the liquid or solution desired to be precipitated by it, so that the precipitant shall tend to settle from the liquor by gravitation. Further, it is necessary to this invention that the solution or liquor to be precipitated shall percolate upward through the mass of solid finely divided precipitant.

In an apparatus with parallel vertical sides the upward flow of liquor would tend to carry off finely divided particles of precipitant unless special means were taken to prevent this. Filters tend to become clogged and are generally useless for this purpose, so that the inventor retains the particles of the solid precipitant, upon whose surfaces the precious metals are in course of deposition, within the apparatus by inducing the subsidence of them. This is effected by continually reducing the upward rate of liquor flow, which is secured by constantly increasing the area of the liquor column as it rises higher in the apparatus.

The apparatus takes the form of a funnel. The liquor enters (under a sufficient pressure or "head") through the bottom orifice. It then meets with and thoroughly mixes with the mass of finely divided precipitant in a condition of suspension in the liquor. The solid, finely divided particles do not sink against the comparatively rapid inflow, or are prevented from doing so to any extent, by means of an automatic valve of ordinary type. By this intimate admixture of liquor with precipitant the deposition of the precious metals in solution in the former is effected upon the minute surfaces of the latter. It now only remains to remove the depleted liquor from the particles of the solid precipitant containing the gold, silver, etc. As the liquor continues its upward flow by virtue of the continually diverging sides of the apparatus the area of the liquor column becomes greater and greater. The rate of the vertical upflow is thereby correspondingly reduced. This continues until a point is reached at which the upflow is vertically so slow that the finest particles are able to settle or subside against it. At any point, therefore, above this limit or "zone," the absolutely clear liquid may be drawn off from the apparatus free from suspended particles and depleted of its precious-metal contents.

If the precipitation of the precious metals be deemed to be incomplete in one apparatus, owing to the richness of the original liquor or to other causes, the outflow may be caused to pass into a second similarly arranged apparatus or through two or more such apparatus placed in series; but in general one apparatus can be made to secure practically perfect removal of the precious metals dissolved in a given liquor by the use of a suitable precipitant. If a series of two or more of such apparatus be employed, the first of the series may be used to enrich quantities of precipitant which have only been partially used up to their fullest capacity of precipitating the precious metals, while the succeeding members of the series are supplied with the necessary amounts of less rich or quite fresh precipitant in order to remove any remaining traces of gold, silver, etc., which may escape unprecipitated in the outflow from the first apparatus. The poorer precipitates in these last apparatus are in course of time removed through the bottom of the apparatus and transferred to the first one of the series, there to be enriched to their full capacity, while their place is taken by fresh quantities of poorer or quite unused precipitating agent, and so on.

When the precipitate is deemed to be sufficiently rich, it is removed from the apparatus by a "three-way cock" at the bottom thereof, or by other suitable

arrangement, and the precious metal it contains finally recovered by any suitable method, such as in the case of the employment of a carbon precipitant by burning, or in the case of the use of a zinc precipitant by smelting.

The apparatus is also supplied with a small central funnel for the introduction of fresh quantities of precipitant from time to time to the point of maximum precipitating action in the apparatus, i.e., near the inflow. By providing this funnel with a bell-shaped or inverted funnel termination a sort of "chamber" is produced in the lower part of the apparatus having an annular space for the passage of liquors between the rim of the smaller funnel and the sides of the large one. This chamber is of considerable aid in promoting the action of the precipitant by keeping the bulk of it constantly near the liquor inflow and securing perfect admixture by means of the vortex currents, etc., it induces. It is further desirable to break up the rapid rush of inflowing liquors at their point of entry into the apparatus and to secure their subdivision and intimate admixture with the precipitant as early as possible. This is effected by capping the end of the inlet pipe with a small perforated cone or "distributor." The perforations may be from one-fourth to one-tenth the diameter of the inlet pipe, but their total area must be larger than that of the sectional area of the pipe. The holes may be bored in a direction perpendicular to the cap cone or they may be made "tangential," i.e., bored at a tangent to the internal circumference of the cone, thus securing a rotary initial flow of the inflowing liquors instead of a series of straight streams. In the majority of cases, however, perpendicular bore holes answer equally well.

The clear precipitated liquor may be drawn off at any point above the limit of subsidence either by a pipe, or, preferably, by allowing it to flow equally over the rim circumference of the apparatus. The latter method secures the quieter and more uniform outflow and does not disturb the top layers of liquor undergoing final subsidence by establishing a quick current in one particular direction.

If desired, the rim may be encircled with a filter-screen of lawn, calico, or other filtering or straining medium, so as to retain within the apparatus any particles of precipitant which may be floated or "buoyed up" by bubbles of air or other gas.

The clear liquors passing over the rim and through the precautionary filter or strainer fall into and are collected by a circular trough or "launder," attached to the apparatus below the rim, whence they are conveyed away by a pipe. As before stated, this may lead into a storage-vat or into another similar apparatus, or, if deposition of the floating particles is not absolutely complete, into any suitable type of apparatus—such, for example, as the slat-partitioned tank used for freeing softened water from traces of deposit—where subsidence is finally rendered absolute. In most cases where the traces of precipitant have escaped, I have secured perfect final subsidence by allowing the liquors to flow through a shallow tank of from four to six times the area of the top of the precipitating apparatus before passing them direct to the storage liquor vats.

Such an apparatus as is described is termed a "precipitating cone." It may be constructed of any suitable material, such as wood, stoneware, galvanized iron, etc., according to the nature of the liquor or precipitant it is designed to treat. Its action, until the charge of precipitant it contains is exhausted and requires renewal, is perfectly automatic and continuous. Its capacity, its height, the angle of its sides, the ratio diameter of inflow pipe to top area of cone will naturally vary with the volume of liquor to be dealt with, the rate and head of liquor inflow, the relation of the specific gravity of the liquor to that of the finely divided precipitant, the actual coarseness or fineness of the particles of the latter, and so on. These data may be calculated or decided by preliminary experiment in any particular case. As an example, however, of the application of this invention to the recovery of gold bullion from cyanide solutions, the following dimensions of the apparatus are cited: For a flow of from 600 to 800 gallons per hour a depth of 5 feet, with a top diameter of 5 feet, is amply sufficient. The diameter of the inlet pipe is from  $1\frac{1}{2}$  to  $1\frac{3}{4}$  inches, according to the head of the inlet liquor, while the perforations of the cap cone or distributor are three-sixteenths of 1 inch

in diameter. The charge of zinc fume in such an apparatus varies from 5 to 30 pounds, according to requirements.

587874—August 10, 1897. E. D. SLOAN. *Barrel-filter*.—The object of this improvement is to provide a suitable filter-barrel, with a durable and highly effective filter, at comparatively low cost. With a view to securing the desired ends the usual trunnioned iron barrel is lined with lead. The framing of the filter-bed is composed wholly of suitable wood capable of fairly resisting the action of chlorine and acids, and which may be filled with suitable matter to enable it to better resist the destructive action of the corrosive solutions. The filtering medium is composed of material which resists the solutions, is well protected against undue abrasion due to the action of the solid matter during the rotation of the barrel, and it has its filtering area supported to enable it to safely bear the overlying contents of the barrel by an underlying floor of such metal as will practically resist the action of chlorine and sulphuric acid—as, for instance, a lead floor—and the latter is freely perforated to admit of the prompt discharge of the filtered liquid. The filtering surfaces are flat, and hence the body of any woven filtering medium is maintained in a condition more favorable to the passage of the liquid than would be the case if it occupied a curved line and said surfaces were concave in conformity with the interior contour of the barrel. The framing of the filter-bed involves inexpensive straight work, as distinguished from the curved or segmental work in framing, which is made to conform to the interior of the barrel as heretofore, and the filter-framing is constructed in parts which are so interlocked as to secure rigidity, but which may be readily applied to or removed from the barrel by way of the usual manhole and without deranging the lead lining or the means by which the lining is clamped to the barrel.

597372—January 11, 1898. P. J. DONOHUE and J. F. CORKER. *Precipitating safe*.—The combination with a closed vessel or standpipe provided with a normally closed outlet at its bottom for the precipitate and having a body or column of zinc filings or like material in its upper part, adapted as corroded to fall into the lower part, of means for supplying, under pressure, the solution containing the precious metal to the lower end of said body or column of filings or like material, to cause the corrosion or oxidation thereof, whereby such corroded or oxidized portions will gradually precipitate to the bottom of the vessel or standpipe and the fresher portions of the filings or like materials be exposed to the ascending solution.

606810—July 5, 1898. J. W. PACK. *Recovery of gold from waste solutions of chlorination works*.—A means for recovering gold from waste solutions of chlorination works, consisting of a tank having an inlet passage at the lower portion and an outlet passage at the upper portion and having metallic aluminum contained therein, and intermediate between the inlet and outlet passages of the tank, and a filter fixed within the tank between the metal and the outlet passage and having its lower side coated with a substance which will arrest the fine precipitated gold and prevent it from passing off with the liquid.

608554—August 2, 1898. R. MOODIE. *Washing or leaching apparatus*.—In an apparatus for washing or leaching, a series of cells, one of which is a dry cell and the others of which contain washing or leaching liquid, means for introducing the material to be washed into the dry cell, an oscillating shaft extended longitudinally of the series of cells, means operated by said shaft to transfer the material from the dry cell to the washing cell next in series, arms attached to the oscillating shaft and extending one into each washing cell, and scoops on said arms.

608945—August 9, 1898. H. B. WILLIAMS. *Lixiviation apparatus*.—In a lixiviation apparatus, the combination of a vertical series of annular tanks arranged one above another and each provided with an exit through which ore or other substances may be discharged into the tank beneath, each tank bottom being provided with an ascending incline leading to one side of the tank exit and having a descending incline on the other side, means for feeding ore into the top-most tanks, pipes for conveying leaching solution into the several tanks separately, the feed of the ore to be continuous and the feed of the solution to be continuous or intermittent, filters located in the several annular tanks, and automatic scraping

and stirring mechanism to cause the ore and solution to be moved around each annular tank and over the filter therein.

**610696—September 13, 1898.** R. AYMER and D. J. NEVILL. *Filter-frame.*—In a filter-barrel, the combination of a rubber grating having a corrugated surface in contact with the curved inner lining and periphery of said filter-barrel adapted to allow the filtering solutions to run along and down the lining of said barrel, a perforated bedplate of glass or porcelain curved concentric with the inner periphery of said barrel and resting on said rubber grating, a filtering medium on said glass bedplate, a curved glass grating resting on said filtering medium, two oppositely disposed cleats secured lengthwise of said barrel to its inner periphery adjacent to the ends of said curved glass bedplate and grating, and wedge keys between said ends and said cleats adapted to key said members against the barrel.

**611515—September 27, 1898.** J. P. SCHUCH, Jr. *Means for extracting precious metals.*—In a metallurgical apparatus for treating ore by a cyanide solution, a tilt-able tank comprising a suitable support, a tank body having a discharge gate at its rear end and pivoted to a support at a point between its centre and the front end, a drain device in the bottom of the tank for drawing off the cyanide solution, holding springs mounted on the support and engaging with the tank body at points between its discharge end and the pivotal connection thereof with the support, and means for retracting the holding springs from engagement with the tank body.

**611935—October 4, 1898.** J. POOLE. *Process of and apparatus for treating ore tailings.*—For the continuous treatment of pulps, slimes, tailings, and the like with cyanide and similar solvent solutions and in combination, a series of shallow tray-like baths, a rake in each bath of the series for reciprocating the rakes, an overflow chute at the end of the series, settling-tanks to receive the overflow from the chutes, means for separately discharging the solid and liquid contents of the tanks, conveyers adapted to raise the solid contents from one tank after discharge, a launder in which such contents are received and in which they may be further treated with a solvent solution or wash, and a further settling-tank for receiving the discharge from the launder.

**615968—December 13, 1898.** T. CRANEY. *Apparatus for treating ores, etc.*—In an apparatus for treating ores, the combination of a tank adapted to contain a body of the ore to be treated, devices for feeding ore into the top of said tank and discharging it from the bottom thereof at a point above the tank in a continuous manner, a solvent supply reservoir, a receiver connections between the tank and said supply reservoir, and receiver for producing a continuous flow of the solvent through the tank in a direction opposite to that of the movement of the ore, an endless-chain carrier in proximity to the tank and having draining buckets adapted to receive the ore discharged from the tank, means for discharging a liquid upon the drainage buckets, and means for collecting the drainage from the buckets and returning it to the aforesaid supply reservoir.

**617029—January 3, 1899.** W. A. KÖNEMAN and W. H. HARTLEY. *Apparatus for separating liquids from solids.*—The method of abstracting liquid from finely pulverized ore, ore slimes, or other solids impervious to percolation with which the liquid is mixed, which consists in subjecting the mixture to gaseous pressure applied above the same, and simultaneously to the action of a partial vacuum applied below the same, removing a portion of the liquid by filtration below the body during compaction of the solids, and collecting and abstracting by pressure the remaining liquid above the compacted solids.

**617497—January 10, 1899.** P. ARGALL. *Cyanide filter-tank.*—In a cyanide filter-tank, a vertical metallic side or wall, a horizontal bottom secured thereto, having a central opening, a packing ring secured to the inside of said wall, near the bottom, with a spacing, a system of level joists converging from the perimeter toward the center, upon said horizontal bottom, a plastic filling between said joists sloping downward from the packing ring regularly toward the central opening, a level floor with interstices laid upon said joists, permeable filtering material upon said floor, and a covering of textile fabric, the outer margin of which is packed into the crevice between the packing ring and the vertical wall.

**618622—January 31, 1899.** P. SOMERVILLE. *Apparatus for extracting metals.*—An apparatus for extracting metals, consisting of parallel barrels having annular

disks closing one end with central inlet openings for the material, a framework and roller support for said barrels, means whereby the barrels are rotated in opposite directions, spiral flanges fixed to the interior of the barrels for advancing the material therethrough, devices for feeding material and fluid matter to the uppermost barrel, means for separating the coarse from the fine material and delivering them separately, and means for transferring material from the discharge end of one barrel into the inlet end of the barrel below.

619211—February 7, 1899. A. M. NICHOLAS. *Filtering apparatus for separating gold- and silver-bearing solutions.*—This invention has been devised for the purpose of providing means whereby solids or insoluble material may be separated from liquids carrying same in suspension, but more particularly for the purpose of providing means whereby the separation of gold and silver-bearing solutions from tailings, slimes, pug, or pulverized ore may be carried on continuously and in such a way that a clean or partially clean filter-cloth will be continuously brought into operation without necessitating stoppages for recharging, as required with the appliances at present in use.

The essential feature of the invention consists in the use of a rotating-wheel, disk, or table formed with a series of air-tight compartments covered with cloth or other filtering material supported upon a metal screen or perforated plate and adapted to be automatically placed in communication with a vacuum pump in turn for a sufficient time to enable the liquid to be drawn through the filtering material, leaving the solid constituents upon the filtering surface, whence they can subsequently be removed by brushes, jets of water, scrapers, or similar contrivances, provision being made for automatically allowing air to enter into the various compartments at the desired period of the operation to facilitate the removal of the solids from the outer surface of the filtering material.

620660—March 7, 1899. J. LUCE. *Apparatus for treating ores by lixiviation.*—In a tank for the treatment of ores, a lining composed of asbestos applied to the inner side of the tank, the notched or recessed boards applied inside of the asbestos, and the steam pipes placed in the notches in the boards, combined with two thicknesses of grooved perforated boards, and the layers of cloth between the boards.

623465—April 18, 1899. G. S. DUNCAN. *Apparatus for separating gold- and silver-bearing solutions from ores or slimes.*—Hitherto upward percolation has been used for the displacement of the various gold- and silver-bearing solutions in the treatment under the cyanide or other similar processes of tailings or free leaching ores which are not in the form of slimes. With this upward percolation false bottoms for the vats with webbing upon them have been used and the solutions have been introduced underneath these false bottoms, which have acted as distributors therefor and allowed them to pass evenly up through the free leaching ore, displacing the gold- and silver-bearing solution contained therein. This false bottom and webbing are adapted for use with free leaching ores only and cannot be employed for displacing solutions used in treating very finely crushed ores or limes which do not leach freely.

The present invention has been devised in order that the various solutions may be displaced, as above described, from finely crushed ore or slimes, without the aid of any false bottom and filtering webbing. And the inventor claims, in an apparatus for separating solutions of the precious metals from residual ores and slimes, the combination with a leaching- and displacement-tank or vat and with a vat to hold said solutions, the latter being placed at a higher level than the former, of a series of pipes to convey said solutions from the higher vat, the discharge ends of said pipes entering the leaching-vat, a series of hoods having slightly arched portions which overlie the said discharge ends, and stirring arms radiating from a central shaft in said vat, the arched portions of the hoods being arranged in radial lines, or at right angles to the movement of currents set up by the stirring arms.

623772—April 25, 1899. A. F. DUEY. *Apparatus for leaching ores.*—A device for treating pulverized ores, comprising a leaching-tank, an air-compressor, a tank for storing the leaching liquid, a perforated pipe in the bottom of the leach-

ing-tank, connections from the air-compressor and liquid-storing tank to the perforated pipe, a perforated drainage pipe in the bottom of the tank, and a layer of filtering material about said pipe.

624533—May 9, 1899. C. H. PEAD. *Slime filter*.—The apparatus consists of a tank fitted with a hood of conical or any other convenient form. The sides of the tank project above the point of attachment of the hood, so as to form an annular space to act as a receptacle forming a launder for discharge of the clear liquid. In the center of the hood is an opening, around which is riveted or bolted a frame or seating arranged to carry a filter composed of one or more layers of filter-cloth or any other well-known filtering medium. The filter is kept in place by means of a protective gird of clamp of suitable form and strength to resist the effective pressure from the interior of the tank. A number of small distribution pipes set at such an angle as to cause the slimes to impinge on the under surface of the filter are connected to the seating of the latter, through which they pass. They are connected to a main distributor, which in turn is connected with the delivery-pipe or column of the slime-pump. One or more taper-shaped plugs or cores constructed of light steel tubes, their number varying according to the size of the tank, pass through the hood and extend to the bottom of the tank. They taper from about 18 inches at the top to 15 inches at the bottom. They are fitted at their upper ends with a flange, to which is attached a shackle. Their lower ends are closed by means of a dished bottom riveted in place and having a strong bolt or stud fitted to its center. Each plug or core rests on a seating fitted to the outside of the hood and through which the plug or core passes. The seating is attached thereto by means of its flange.

In the bottom of the tank and directly under the aperture in the hood through which the plug or core passes is a discharge door of the ordinary manhole or other convenient type. The end of each plug or core passes easily into the discharge opening, and the discharge door is drawn up onto its seating or joint by means of the bolt or stud on bottom of the plug or core and by its nut. The plugs or cores when in place and holding up the manhole doors afford an effectual means of resistance against internal pressure.

A special pipe is arranged and fitted to the upper portion of the tank to drain the space forming a launder between the top of the tank and the upper surface of the hood and to conduct the liquid portion which has passed through the filter to the precipitation boxes or to waste.

624633—May 9, 1899. F. A. EDWARDES. *Apparatus for use in treating metallic ores*.—In apparatus for use in the treatment of metallic ores, the combination with an annular vat having a stirrer moving therein and skimmers attached to and moving with the said stirrer, of means for tipping the said vat for discharging the contents.

624957—May 16, 1899. L. H. MITCHELL. *Tank-bottom discharge door*.—A discharge apparatus for tanks provided with a hollow upper portion, a base having integral-bearing zones connected thereto at one end thereof, a casting having an upper annular supporting rim and adapted to receive said bearing zones, a ring surrounding said casting, devices connecting said rim and ring to secure the casting in position, and means supported by said casting to unseat said base.

624958—May 16, 1899. L. H. MITCHELL. *Tank-bottom discharge door*.—A discharge apparatus for tanks consisting of a casting secured in the bottom of the tank, a ring below the tank around the casting, and means for securing the rim and ring in position, a funnel above the casting, a base connected with the lower end of the funnel and provided with an annular offset or shoulder, a packing-ring within the offset, and adapted to rest upon the rim of the casting, a plate or bar bearing against the rim of the casting, a nut-carrying screw in the plate or bar adapted to engage the base and draw the same within the casting, a brace or clamp connected to the plate or bar above the nut on the screw, and means for rotating the screw.

639540—December 19, 1899. W. DUNCAN. *Means for mixing and aerating sands or tailings while under treatment by solvents*.—Numerous attempts have from time to time been made to secure the thorough mixing of sands and tailings, includ-

ing slimes, with the solvent while under treatment and also to prevent that close packing which prevents the percolation of the solvent and wash liquors. For this purpose vertical vessels with vertical agitators, revolving barrels, and air, steam, and water jets have been used, but these means have not been as efficient as they might be.

This invention relates to improved mechanical means for mixing and aerating "sands" or "tailings," by which terms are included slimes, sludges, and concentrates, while under the action of solvents, whereby time is saved and a better extraction is obtained; and it consists of a semicircular vat provided with a revoluble agitator composed of arms arranged helically on a shaft running the length of the vat. At one end of the vat is placed the fast and loose pulleys and gear for slowing and rotating the agitator, while at the opposite end a series of taps are provided connected to the vat at various heights and to pipes, so that the liquor can be drawn off at any desired point and either run direct to the sump or through a filter to the sump.

641419—January 16, 1900. H. C. WHEELER. *Agitator*.—In an agitator, the combination of the vat, the track provided with the cog-rack, the carrier provided with the pinion meshing with the cog-rack, the first driving-shaft provided with the driving-pinion, the driven cog-wheel meshing with the driving-pinion, the gear-wheels connecting the driven cog-wheel with the pinion meshing with the cog-rack, the agitator-frame journaled or pivoted to the carrier-frame, the second driving-shaft journaled in the agitator-frame, the agitators journaled in the agitator-frame and adapted to be operated by the second driving-shaft, intermediate gearing connecting the second driving-shaft with the driven cog-wheel, one of such gears being journaled with its axis in line with the axis of the pivotal support of the agitator-frame, and means for rotating the first driving-shaft.

647358—April 10, 1900. D. W. BALCH. *Leaching-tank*.—A tank having a bottom, a leaching false bottom above the same, and vertical filtering partitions arranged in pairs within the tank, whereby spaces are left between pairs of partitions, and other spaces are left between members of such pairs, said spaces last named all communicating with the chamber between the bottom and false bottom.

647678—April 17, 1900. C. W. MERRILL. *Means for charging leaching-vats*.—This invention relates to a method of charging ore or tailings to a leaching-vat, which process is a step in the treatment of said ore or tailings preliminary to the application of the solvent solution in cyanide, hyposulphite, or other hydrometallurgical processes.

It consists essentially in conveying the tailings or ore by any well-known adaptable mechanical means to a point above the center of the vat to be charged and delivering the material there to a hopper, which feeds a revolving chute inclined at an angle greater than the natural slope of the material to be handled, and with openings adjustable both as to size and position, through which the material to be treated falls gently into the vat and distributes evenly, thus giving a charge of minimum density and maximum homogeneity, the conditions most favorable to successful leaching and dissolution of the precious metals.

The ordinary method of charging leaching-vats is from cars running on a superimposed track. By this means the momentum of the carload of tailings or ore dropping through five or more feet to the bottom of the vat is such as to produce considerable packing and, moreover, an uneven packing or density. For instance, in dumping from an end discharge car the resultant mass of ore or tailings will take the form of a cone in the vat and the maximum density will be in the center of the approximate circle forming the base of the cone and will decrease along the radii toward the circumference of this circle. Furthermore, the variation in fineness of the different carloads is not equalized, and a vat charge of ore or tailings results, which is heterogeneous, both as regards density and as regards fine and coarse material. Now, first, the charge of ore or tailings in a vat should be of the least density possible to obtain, because experience has demonstrated that the greater the permeability, and consequently the greater the amount of lixiviant possible to percolate through the charge, the greater the extraction of the precious metals in a given time, or, from another standpoint, the greater the permeability the less the economic period for leaching, and hence the less the cost for plant



and subsequent operation; second, the charge should be as nearly homogeneous as possible as regards both density and size of material, because in leaching ores it is necessary to follow solution with wash-water to replace and prevent the loss of the former or to follow one lixiviant with another of different strength or containing a different solvent, and in doing this to maintain the surface of demarcation between the one and the other as nearly a horizontal plane as possible in order to minimize the mixing of effluent solutions. The above conditions of minimum density and maximum homogeneity are produced by means of a revolving inclined wide chute with small openings in the bottom, adjustable as to size and position transverse to the direction of the stream of ore or tailings. By means of this method a number of very small streams of ore or tailings fall gently into the vat as the chute revolves, and by increasing the speed of revolution a carload of fine or coarse material can be spread over the whole area of the vat, thus giving the smallest possible dimension parallel with the course of the lixiviant.

653631—July 18, 1900. J. C. WALLACE. *Filter barrel or tank*.—In a filter barrel or tank, a filtering device consisting of a series of curved metal plates, perforated, fastened to the inside wall or walls of said barrel or tank; a filter-cloth upon the upper surface of said plates, secured thereon by a series of imposed metal bars and filling strips secured in position by bolts or other fastening devices to the wall or walls of said barrel or tank.

653684—July 17, 1900. F. H. LONG. *Metallurgical filter*.—The combination with a closed vessel having a filter septum and a regulated outlet port for the filtrate beyond such septum, of the wash-water pipe connected in hydrostatic column with said vessel and the external centrifugal pump joined at its separate sides in closed union with the opposite ends of the vessel, the journal-box for said pump-axle being furnished with a water column pipe to counterbalance the hydrostatic pressure at the vessel.

654315—July 24, 1900. T. E. LEECE. *Apparatus for working ores of valuable metals*.—This invention relates to an apparatus which is designed for working the ores of valuable metals, and is especially useful for separating slimes from solutions in which they may occur, and also for separating heavier and lighter parts under any condition in which they may be found associated.

It consists essentially of a tank and an endless traveling belt with directing rollers, by which one portion of the belt is caused to travel through the tank in close proximity with the bottom and the other part is guided back exterior to the tank by similar rollers. It also comprises a means for straining or separating the liquid from the heavier portions.

660498.—October 23, 1900. J. A. FLEMING. *Apparatus for leaching ores*.—In an ore-leaching apparatus the combination with the leaching-tank having a pulp discharge, of the conical perforated filtering-hopper therein having the discharge for the pulp, means by which to maintain air pressure below the diaphragm, whereby to control the flow of solution through it, means for the introduction and withdrawal of chemicals to and from the body of the tank above the filtering diaphragm, and devices for controlling the discharge of the pulp from the tank.

660499.—October 23, 1900. J. A. FLEMING. *Apparatus for leaching ores*.—An ore-leaching apparatus, consisting of the leaching-tank, having a filtering-hopper a solution discharge below said hopper, and a pulp discharge also below said hopper, and independent of the solution discharge, a washing-tank below the leaching-tank and in position to receive the pulp from the discharge thereof, and means for controlling the passage of the pulp from the leaching- to the washing-tank.

664059—December 18, 1900. J. P. SCHUCH, Jr. *Ore-mixing machine*.—Heretofore, in treating gold-bearing ores by the common cyanide process, the ore is first crushed, dried, and rolled to a proper degree of fineness, and that which requires roasting is then conveyed to the roasters, while the oxidized ore, which does not require roasting, is conveyed to the bin or receptacle therefor. After the portions of the ore to be roasted have passed through this step of the process the same is conveyed to the cooling-room before being deposited in the bin or receptacle referred to which contains the ore requiring no roasting. All of the ore

is then removed by manual labor into the ordinary stationary cyaniding-tanks, and after these tanks are filled with the ore the cyanide solution is introduced therein. In this process the filled cyanide-tanks, with the solution and ore therein, are permitted to remain filled and unmolested for a sufficient length of time for the solution to act on the ore, after which the gold-bearing solution is drawn off and allowed to flow to the precipitation-room, while the tailings in the tank are then washed with water and shoveled out or sluiced out when this is possible. In this process, which is the one usually followed out in extracting gold and silver from their ores by the use of cyanogen containing solvents, the percentage extracted rarely exceeds 80 per cent. of the ore value, and it is the purpose of the present invention to provide means whereby a larger per cent. of the value of the ores may be saved.

To this end the invention contemplates an improved mixing-machine which provides for a thorough aeration of the ore and solution, while at the same time providing for a mixing of various grades of ore with the cyanide solution, so as to make one even grade out of ores of various values. And the inventor claims, in an ore-mixing machine, an open tank provided at the bottom with a solution drain, a perforated false bottom arranged within the tank above the main bottom and supporting filtering material, an ore discharge pipe communicating with the interior of the tank immediately above the plane of the false bottom, a revoluble agitator depending within the tank into close proximity with reference to the false bottom, and a plurality of air jets arranged to communicate with the tank in a plane intermediate the said false bottom and the lower end of the agitator thereabove.

664196—December 18, 1900. J. C. WALLACE. *Filter-bed*.—In a filter-barrel, a filter-bed consisting of a series of metal plates having drain slots or perforations therethrough, a series of perforated tiles arranged as a filtering medium upon and supported by said metal plates, a series of metal-binding strips imposed upon or against said tiles; together with suitable means for fastening or confining the same together and to the inner wall of a filter-barrel or tank.

671028—April 2, 1901. J. R. PHILLIPS. *Pulp agitator*.—This invention consists of an inclined or funnel-shaped tank or containing vessel into which the pulp is placed with water, cyanide solution, or other equivalent liquid, a circulating- or suction- and force-pump by which the surface liquid may be drawn from the tank, and a pipe extending centrally down to near the bottom of the cone, with a discharge nozzle through which the liquid is delivered with force, so as to flow upward along the sides of the funnel and through the material, whereby the latter is loosened, agitated, and prevented from packing. In conjunction with this may be used a canvas or equivalent filter lining for the funnel, with means for providing a space intermediate between it and the sides of the funnel for the filtering through of water, and a means for conducting such filtered water away from the apparatus.

680154—August 6, 1901. A. D. JANSEN. *Discharge door for cyanide-tanks*.—In cyanide treatment the sands are subjected to the action of cyanide solution, which solution after the proper length of time has elapsed is drawn off through a filter composed of matting or some similar material situated at the bottom of the tank. This matting or filtering material does not rest directly on the bottom of the tank, but is supported by a grating or perforated false bottom in order to allow a free passage for the solution which has filtered through. That portion of the tank, therefore, which is situated over the discharge door has no grating or filtering material, and consequently a more or less vertical column of sand is left in the tank, which still contains cyanide solution with gold in solution, the result being that this portion is imperfectly treated.

The object of this invention is to provide a door so constructed that a piece of matting or filtering material may be placed upon it in order that the filtration of the solution shall be just as complete over the discharge door as in the rest of the tank.

This invention furthermore relates to an improved construction, whereby the door is rendered much more easily closed and also to a system of packing the same by which joint between the door and the bottom of the tank is rendered tight.

683412—September 24, 1901. A. J. PERRY. *Ore-separator*.—The object of this invention is to introduce a mixture of steam and air in the pulp, whereby the precious metal receives a quick chemical action, with the result that considerable time is gained over the method heretofore employed. And the inventor claims, in a leaching apparatus, the combination of a receptacle for holding pulverized ore, an agitator mounted in said receptacle and having a series of radial horizontal pipes each provided with a series of perforations at one side thereof, a series of scrapers or blades mounted on said agitator, a pipe adapted to supply to said agitator a mixture of steam and air from a proper source, and means adapted to rotate said agitator whereby the discharge of steam and air through the perforations of said pipes is directed toward the rear while the said scrapers or blades are moving in the opposite direction.

684654—October 15, 1901. C. VOELKER. *Ore-filter*.—The extraction of valuable metals from ores through the lixiviation processes, such as the cyanide and others, although allowing the advantageous working of low-grade ores, still has one fault, that more or less metal remains in the tailings, and thus losses occur caused by the slimy particles contained in the pulverized ores generated from clay, talc, and other minerals which clog up the meshes of the filtering-cloth, and thus prevent the solution from going through freely. In such apparatus the ore is introduced and the solution added, and where it happens that the ore lies in different grades of value inside the tank, the solution cannot dissolve the metalliferous particles in an even manner, and at the same time where it enters first it will affect the pulp more thoroughly, and as it goes down to the bottom will take the slimes forming with it, depositing them around the aperture through which the solution is drawn off, and even several after-leachings will not remove them. To overcome these drawbacks it is necessary to construct a mechanical apparatus which shall possess the condition of letting the soluble liquids needed to dissolve the metals go through the pulp in a space of time to be governed by the operator. Some ores are liable to contain chemical substances retarding the effectiveness of the soluble agent used, and where it is of great import to remove them as quickly as possible to keep them from going into chemical action with the solution used.

The object of this invention, therefore, is to combine the above-mentioned conditions, and the apparatus can be used, in addition to other milling-plants, to receive the tailings direct from the mill. The filtrate can be examined in regard to the valuable mineral matter which may exist, giving the metallurgist the means of saving the valuable salts of mercury, copper, silver, gold, and the like which may form through the chemical or electrical action in the amalgamators where such are used and where the extravagant use of copper sulphate, mercury, and salt is in most cases the cause of the solubility of gold.

The inventor claims: An ore-filter, comprising a funnel-shaped tank, a basket- or filter-holder removably arranged in said tank and fitting closely against its inner wall, a filtering textile stretched over the inner surface of said basket, a top or hood for the tank, a shaft extended downward in the tank, and a screw mounted on said shaft and spaced at its inner edge therefrom, the said screw having the end of its upper turn turned downward.

687920—December 3, 1901. A. D. JANSEN. *Apparatus for charging or discharging cyanide-vats, etc.*—In combination, the pair of tanks situated one above the other, stirring mechanism for said upper tank, having a hollow supporting or operating mechanism, and stirring mechanism in said lower tank, having its operating mechanism in line with the hollow mechanism of the upper tank, and means for raising said operating mechanism of the lower tank into said hollow mechanism of the upper tank.

688085—December 3, 1901. A. G. GOLDSOBEL, W. MUTTERMILCH, and C. JABLONZYNSKI. *Apparatus for the recovery of precious metals from photographic residuum*.—The combination with a vessel having a loose lid, a spout or outlet for the outflow of liquid and a conical bottom and with a precipitating material contained in said vessel, of a tube having a funnel-shaped end reaching within said vessel, and of a second tube provided with a cock connecting the aforesaid precipitating vessel and funnel-shaped tube with a second vessel or receiver.

689799—December 24, 1901. R. L. GRAVES. *Ore-leaching apparatus*.—The apparatus for use in extracting ores, consisting of a plurality of tanks, a pump, a discharge-pipe leading from said pump and having a plurality of branches leading to the several tanks and provided each with a discharge-pipe which may be turned axially or swung vertically, valves controlling the several branches, and a flexible supply- or suction-pipe leading to the pump and arranged to be shifted from tank to tank, levers connected with the several discharge-pipes whereby they may be turned axially, and means connected with the lower ends of the discharge-pipes whereby they may be swung vertically.

690375—December 31, 1901. G. RUBSCH, Jr. *Agitating-machine for cyaniding*.—An agitating-machine for the treatment of gold and silver ore by the cyanide process, comprising an agitating-tank, having a conical bottom; a heating-chamber surrounding the conical bottom of the agitating-tank; means to heat said chamber, a rotary pump, centrally disposed in the agitating-tank, adapted to take the solution from the bottom of the tank and discharge it above the top thereof; a rotary deflector, adapted to distribute the solution over a stationary deflector; and a stationary deflector affixed to the casing of the pump, adapted to deflect the solution to near the edge of the agitating-tank.

691706—January 21, 1902. F. H. LONG. *Metallurgical filter*.—The combination of a vessel having a conical filter-septum and an outlet-port for the filtrate beyond such septum, of means for establishing an end-to-end circulation of the vessel contents above said septum, a conical spreader and an oppositely facing conical baffle-plate having a projecting spiral flange successively interposed between the ends of the vessel and arranged adjacent to said conical filter-septum to intimately direct such circulation over the surface thereof.

697178—April 8, 1902. E. L. SHARPNECK. *Apparatus for the treatment of ores*.—As a means for facilitating the dissolving of the values in ores, the combination of a leaching-tank, a conduit leading from and discharging directly into the tank, and means in the conduit connected with the heating-medium supply for agitating, circulating, and heating the liquid contents of the tank.

698016—April 22, 1902. J. J. HERVEY. *Cyanide-tank*.—Cyanide-tank having a tapering bottom and a central cone arranged in connection with the bottom, an annular lining arranged in the tank and open at its lower end, a filtering-screen connecting the lower end of the lining and the central cone, the air and water-pipes, the charging- and discharging-pipes, and the forcing means connected with said pipes.

699211—May 6, 1902. DE W. C. MOSHER. *Barrel-filter*.—The combination with the lead lining of a filter-barrel, of filter-sections or plates having projections on their outer sides and perforations through the plates between the projections, and having bent ends, whereby the plates may be united to the lining by burning.

699212—May 6, 1902. DE W. C. MOSHER. *Barrel-filter*.—The combination with the lining of a filter-barrel, of perforated filter-sections, and means for supporting said sections and securing them to the linings, said sections having their adjacent ends so constructed and arranged to form a longitudinal channel.

701239—May 27, 1902. F. D. WOOD. *Means for working ores by the cyanide process*.—An apparatus for treating ores consisting in combination of a plurality of aligned containing-tanks, a transversely concaved endless belt passing through and returning beneath each of said tanks, and upon which the ore is carried each of said belts discharging its load upon the belt of the next succeeding tank, means for driving said belts in unison, means by which said belts are kept transversely distended, and rollers disposed at intervals in said troughs and over which the belts pass, whereby the latter are given an undulatory movement.

702064—June 10, 1902. F. H. LONG. *Metallurgical filter*.—In metallurgical filters, the combination with the closed perforated tank having an internal fabric-septum with stretcher-frame therefore to rest against the tank-walls of the feed-pipe leading into the tank-bottom and the separate wash-water pressure-tube united to said feed-pipe between the inlet and outlet valves thereof.

702490—June 17, 1902. R. SEEMAN. *Apparatus for treating copper ores*. A plant for the treatment of ores, comprising a safety vessel, a mixer revolvably

mounted, a settler revolubly mounted at a lower level than the mixer, and a still revolubly mounted at a lower level than the settler, and pipes connecting the several vessels together, the portions of the several vessels and pipes with which the ammoniacal solution of copper comes in contact being of material indestructible by such solution.

705589—July 29, 1902. A. JAMES. *Apparatus for precipitating gold and silver from their solutions.*—In the precipitation of gold and silver from cyanide and other solutions zinc is usually employed as a precipitant, and the use of iron vessels containing the solutions has been found objectionable, because the iron being electronegative to zinc a galvanic action is set up between the vessel and the zinc, which causes the precious metal to be deposited upon the vessel instead of upon the precipitant. Owing to this difficulty the general practice has been to use vessels constructed of wood or earthenware, which are inconvenient and do not facilitate the cleaning-up operation.

The object of this invention is to avoid these objections.

To this end the invention consists in a metallurgical filter for separating precious metal from a solution containing it, consisting of a metallic vessel and a zinc sponge disposed therein, said vessel having an inner coating of enamel, whereby galvanic action between the metallic vessel and the zinc is prevented and deposit of precious metal on the vessel avoided.

705726—July 29, 1902. J. C. WALLACE. *Filter-bed.*—In a filter-bed, the combination of a corrugated filter-sheet or blanket having numerous perforations through the lower arcs of said corrugations; a series of transverse supporting bars formed to fit under and receive the corrugated contour of said filter-sheet; a series of superimposed binding strips or bars with transverse corrugations and slotted ends; two longitudinal side binding strips or bars, and bolts adapted to holding the several members together and in place within a filter-barrel or tank.

706334—August 5, 1902. G. MOORE. *Apparatus for leaching ores, etc.*—In dissolving the soluble portions of ores, furnace products, and other like materials it has always been difficult in one operation to dissolve the final traces of the soluble portions and at the same time completely utilize the dissolving power of the acid alkali. The weakening of the acid or alkali by its dissolving action makes its action less energetic toward the finish of the operation at the very time when the more difficult soluble particles needing the most energetic dissolving action are acted upon. This not only causes loss of reagent, but also further loss on account of the poor extraction of the soluble elements desired. Also, in the case of ores of a talcose or slimy nature the talcose portions in the form of slimes prevent percolation of the solutions in tanks by clogging. These slimes should be separated and filtered separately by known methods. Then the remaining portion will easily allow percolation.

The object of this invention is to provide an improved apparatus for the purpose of overcoming these difficulties; and with this object in view the invention consists, primarily, in a hollow truncated cone mounted to rotate about a central horizontal axial line, provided with an opening at one end to receive the material to be acted upon, an opening at the opposite end to receive the fluid solvent, means for actuating the material through the cone in one direction and means for actuating the fluid solvent through the cone in the opposite direction simultaneously with the passage of said material.

706472—August 5, 1902. A. E. JOHNSON. *Filter-bed for chlorination barrels.*—The combination with a chlorination barrel or tank of a filter-bed placed therein and composed of a series of bars placed side by side and having grooves in their sides forming spaces for filtering material, the corners of the bars being cut away to permit insertion of the filtering material after the bars are placed side by side, and binding strips located at the ends of the bars and covering the filling openings, the said strips being secured to the barrel to hold the filter in place, an outlet being formed in the barrel below the filter.

708494—September 2, 1902. J. RANDALL. *Apparatus for extracting metals from ores.*—In an apparatus for treating ores, the combination of a series of tanks

with a series of agitators above said tanks and discharging into the same, so arranged that the overflow of the solvent fluid from each tank discharges into the agitator over the next adjacent tank and from thence into the latter, and means for conveying the ore from the bottom of each of said tanks into the agitator directly above the adjacent tank for discharge into the latter.

709135—September 16, 1902. J. BROWN. *Ore-leaching apparatus*.—An apparatus for leaching ores, comprising a tank adapted to contain water or other liquid, a conduit connected to and extending upwardly from the tank and having the plurality of chambers, a hopper disposed above the upper chamber, ball-valves for controlling the discharges of the chambers and hoppers, electromagnets disposed above the valves and adapted when energized to raise the same, the hoods and deflectors arranged in the chambers and hopper above the electromagnets, an electrogenerator, a movable commutator and circuit wires connecting the magnets, generator and commutator, the said commutator being adapted to change the circuits and the condition of the magnets.

709593—September 23, 1902. D. C. BOLEY. *Apparatus for treating pulverized ores of gold and silver*.—The difficulty which has been experienced in treating finely divided ores by filtration with a cyanide solution is well known. In the case of battery slimes, which are produced by crushing the ore in the battery in the presence of either water or a cyanide solution, and equally in the case of the fine dust which is produced by dry crushing and which becomes a slime by the addition of moisture, the difficulty in all these arises when attempt is made to filter the material, so as to draw off the moisture, because the slimes collect upon the surface of the filter, and when this collection reaches a certain thickness the fluid will no longer pass through and the filtering surface must then be cleaned, and this difficulty begins very soon and constantly increases as the filtering proceeds. Attempt has been made to overcome this to some extent by producing a vacuum at the delivery side of the filter, and also an attempt to facilitate the filtration by creating an air pressure on the other side of the filter; and it has been attempted to prevent the collection of this impervious coating of filtrates by stirring and agitating the contents of the filter. So far there has been no organized apparatus capable of carrying on this work of filtering slimes successfully and economically, and such an organized apparatus is the object of the present invention, which consists in a revolving filter cylinder having vacuum chambers and means for supplying air pressure, the filtering surface being arranged in cylindrical form inside of the vacuum chambers, and the mode of operation being to agitate the pulverized ore by revolving the cylinder and by the pressure of compressed air, and dissolving the gold and the silver in the presence of a solution of potassium cyanide and of the oxygen derived from the compressed air, and the removal of the solution containing the gold and silver by filtration, assisted by the vacuum, and the continuous removal of the filtrates from the surface of the filter by their own gravity in the turning of the cylinder, and the further cleaning of the filter surface by a backward blast of compressed air applied after the filtering there-through ceases.

710462—October 7, 1902. R. D. JACKSON. *Settling-tank*.—In a settling-tank, a distributor having downwardly extending discharge outlets for pulp and liquid, means for supplying material to said distributor, means for rotating said distributor, and means for raising said distributor while rotating, whereby the distributor rises steadily above the accumulating deposit.

710495—October 7, 1902. S. T. MUFFLY. *Apparatus for treating ores*.—An apparatus for treating ores, comprising a rotary cylinder, air-inlet and outlet pipes connected therewith at opposite ends thereof, automatic valves oppositely directed and controlling the inlet and outlet pipes, means for forcing air through the said inlet pipe, means for heating the said air, a solvent container connected with the air-inlet pipe whereby the solvent is forced by and with the air into the rotary cylinder in the form of a spray, means for governing the amount and pressure of air and of the solvent, devices within the cylinder for scattering and agitating the ores as the said cylinder is revolved.

711236—October 14, 1902. H. SMITH and P. C. BROWN. *Apparatus for use in extracting precious metals from their ores*.—In a lixiviation apparatus, a revoluble-

tank, pipes conducting a solvent air, and steam to the tank, means for rotating the tank, and a pipe in the end of the tank opposite the end containing the supply-pipe.

**712963—November 4, 1902. J. J. PRINDLE. Barrel-filter.**—In a chlorination barrel-filter, a platform comprising a series of perforated members or sections having the end portions thereof thickened or enlarged, said enlarged portions provided on their lower sides with prolonged curved faces forming supporting heels which conform to the curvature of the barrel in which the filter-platform is adapted to be used, and bolts passing through said curved heels and co-operating therewith in holding the platform in place.

**713694—November 18, 1902 J. P. SCHUCH, Jr. Ore-mixing-machine.**—An ore-mixing-machine, comprising the following elements: An ore-mixing-tank, a false bottom including a strainer, means for discharging air beneath the strainer to keep the meshes thereof free from any accumulation of slime or the like, air supply-pipes disposed above the strainer to effect aeration of the contents of the tank, a track carried by the upper outer portion of the tank, an agitator-shaft having its upper portion polygonal in cross-section, a spider having a hub engaging the said polygonal portion and carrying traveler-wheels at its extremities to engage the track, agitator-bars suspended from the spider, and beaters or stirrers carried by the bars, each set of beaters being disposed in break-joint order with relation to the adjacent set of beaters.

**714822—December 2, 1902. J. RANDALL. Settling-tank or decanting vessel.**—A settling-tank, consisting of a body having a vertical side and a bottom formed of slopes of different inclinations and provided with a central outlet, the said side having a cutaway portion forming an overflow lip, a launder encircling said lip and provided with a discharge-spout, a baffle-plate of cylindrical form connected by strips to the upper portion of said side and extending into the tank below the top and nearly to the lower edge of said side, and a pipe leading from said central outlet.

**718680—January 20, 1903. B. TULLY. Barrel-filter.**—A filter, comprising a rotatable barrel, provided with a lead lining, the body of the barrel being provided with apertures and the lining being perforated opposite said apertures, a lead launder arranged on the exterior of the barrel and provided with a plurality of lead branch pipes, said branch pipes at their inner ends being fitted in said apertures and connected to the lead lining about said perforations.

**719273—January 27, 1903. Z. B. STUART. Apparatus for treating ores.**—A tank having an open top and a concave bottom formed of perforated removable plates, a removable, conical plate upwardly projecting from the center of the bottom, a perforated box under said conical plate, a layer of coarse fabric surrounding said perforated box, a filtering material under said perforated plates, a pump, a suction-pipe extending from said pump to and through the mixture in said tank to a point adjacent to the upper surface of the mixture, and a discharge-pipe extending from said pump to a point adjacent to the conical part in said tank, a vacuum-tank, a pipe connecting said vacuum-tank to said perforated box, and a suction-pump connected to said vacuum-tank.

**719664—February 3, 1903. J. B. HEFFERNAN. Chlorination barrel.**—In a chlorination barrel a parallel series of pipes having numerous small orifices through their longitudinal walls, one or more headers adapted to receiving the ends of said pipes, a valve or valves connecting said header or headers with an outside source of fluid pressure.

**719768—February 3, 1903. S. C. C. CURRIE. Mechanism for mixing and storing liquids and gases for ore treatment.**—In combination, an alkali mixing-tank, an alkali stock-tank at a lower level and connected by a pipe thereto, a mixing-chamber at a level below the alkaline storage-tank, said mixing-chamber having inclines leading from opposite sides, a chlorine gas supply-pipe leading from above the top of the mixing-chamber into the bottom thereof, a storage-tank for chlorinated liquid below the level of the mixing-tank, and a gas supply-pipe leading from the top of the mixing-chamber nearly to the bottom of the storage-tank.

**722314**—*March 10, 1903. L. H. MITCHELL. Discharge means for tanks.*—A discharge apparatus for tanks, provided with a casting having an upwardly projecting rim provided with shoulders having longitudinally inclined under faces, a funnel having a base provided with a depending offset portion, a gasket mounted in the recess formed by said offset portion and adapted to seat upon the top of the rim, lugs formed on the depending portion and provided with longitudinally curved upper faces to engage the inclined faces of the shoulders, and operating handles at the top of the funnel.

**722399**—*March 10, 1903. H. R. CASSEL. Barrel-filter.*—A barrel-filter composed of a barrel having a lead lining, and of a filter having rigid cores and surrounding lead casings made integral with the lining.

**725549**—*April 14, 1903. H. R. ELLIS. Centrifugal lixiviating-machine.*—In a centrifugal filtering-machine, the combination of a rotary-shaft, a drum mounted thereon, a perforated partition within the drum, arranged concentrically with the periphery of the drum at such distance therefrom as to form an annular chamber about the perforated partition, means for supplying liquid to the annular chamber, a discharge opening in the bottom of the drum, a cover therefor adapted to be held open by centrifugal force when the drum is rapidly rotated to permit discharge of the charged liquid, and to be held in closed position when the drum is rotated slowly, and a discharge-gate in the bottom of the drum at a point nearer the center than the discharge opening.

**727230**—*May 5, 1903. F. G. UNDERWOOD. Leaching-tank filter.*—The apparatus consists of a tank having a central discharge aperture provided with a movable closure, an interior filter diaphragm spaced from the bottom of the tank and having a central discharge aperture registering with the tank-discharge aperture and provided with a movable closure, in combination with vertical filter members radially disposed and spaced apart between said discharge apertures and the walls of the tank and communicating with the space beneath the diaphragm.

**727368**—*May 5, 1903. H. HIRSCHING. Apparatus for treating ores.*—An ore-treating apparatus including a leaching vessel, a settler, a filter, a still, a condenser containing a coil, a stock-solution-tank, and an absorption-tank, said absorption-tank consisting of an outer casing communicating with a cooling-water-tank, an inner casing spaced from the outer casing and communicating with the stock-solution tank, and an innermost casing spaced from the inner casing and communicating with the coil of the condenser, whereby the vapors and fluid emerging from the coil are caused to flow through the innermost casing and through the absorption water, and the absorption water is caused to flow through the inner casing to the stock-solution-tank, said parts being connected together by means of pipes.

**728126**—*May 12, 1903. P. W. McCaffrey. Precipitating apparatus.*—In precipitating apparatus, the combination of a tank having curved walls, said tank being adapted to hold the solution to be treated and being provided with a central partition around the extremities of which the liquid is free to circulate, blocks or pieces made fast to the opposite sides of the tank, their inner surfaces being parallel with the surfaces of the partition, and cylinders mounted to rotate on opposite sides of the partition and partially immersed in the solution, said cylinders being perforated and containing scrap iron, the ends of the cylinders being located as close to the partition and the said blocks as is practicable in order to allow perfect freedom of movement, and means for rotating the cylinders in reverse directions whereby the liquid is set in motion in a circular current.

**728746**—*May 19, 1903. P. W. McCaffrey. Means for precipitating dissolved metals.*—In precipitating means, the combination of a tank adapted to hold the liquor from which the precipitation is to be made, a number of perforated cylinders containing scrap metal, said cylinders being mounted to rotate in said tank which is constructed to receive solution at one end and discharge it at the opposite end above the lowest part of the cylinders, the latter being arranged in successive order from the feed to the discharge extremity of the tank and partially immersed in the solution, and suitable means for producing a current of liquid through the tank from end to end, whereby the contact of the liquid with the scrap metal in the tanks is facilitated



**729805—June 2, 1903.** J. STOVEKEN and L. STOVEKEN. *Apparatus for extracting metals from ores.*—In an apparatus for extracting precious metals from their ores, the combination of a tank for containing a cyanide or other suitable solution, means for reducing ore to a finely divided or comminuted state, one or more conduits connected with the solution-tank and arranged to supply the ore with solution incident to the reduction thereof, means for agitating and mixing the ore and solution, arranged to receive the same from the reduction means, a filter arranged to receive the ore and solution from the agitating and mixing means, and adapted to separate the solution from the ore, one or more decanting-tanks arranged to receive the solution or solutions from the filter, a precipitating-tank which receives the clear solution from the decanting-tank or tanks, and means for transferring the solution from the precipitating-tank back to the solution-tank.

**729806—June 2, 1903.** J. STOVEKEN and L. STOVEKEN. *Agitation-tank.*—The combination of a tank, a central, vertical, cylinder arranged therein, a piston movable in the cylinder and having a rod extending through the upper head thereof, a gear disposed above the tank and adapted to be connected by a driving connection with a motor, a shaft stepped on the piston-rod and keyed to and adapted to move vertically through the gear, wings connected to and extending inwardly from the vertical wall of the tank, agitating means carried by the said shaft and surrounding the upper end of the cylinder, and comprising a head fixed on the shaft, blades disposed below the wings and connected together, said blades being curved in the direction of their length and inclined in the direction of their width, connections between the outer portions of the blades and the head of the shaft, connections between the inner portions of the blades and said shaft, and a pipe communicating with the cylinder below the piston and adapted to be connected with a source of fluid-pressure supply.

**730195—June 2, 1903.** J. STOVEKEN and L. STOVEKEN. *Metallurgical filter.*—In an apparatus for extracting precious metals from their ores, the combination of a filter comprising a frame, an endless filter-cloth, means for driving same, means for pressing pulp against the upper stretch of the cloth at different points and separate receptacles arranged below the cloth at such points, and a decanting-vat having separate tanks connected with the said separate receptacles of the filter; the said separate tanks communicating with the vat at their upper ends, and having valved discharges at their lower ends.

**730384—June 9, 1903.** W. H. MOTTER. *Agitating apparatus.*—The combination of a rocking platform, means for operating the same, a frame mounted to reciprocate adjacent to the platform, cylindrical tanks or vats trunnioned on the frame and engaging the platform, flexible devices connected with the opposite extremities of the frame, guides therefor, a liquid containing-tank, a piston therein, stems protruding from the opposite extremities of the tank, and a valve-controlled conduit connecting the opposite extremities of the tank, the flexible devices of the frame being connected with the piston stems.

**730385—June 9, 1903.** P. W. McCAFFREY. *Apparatus for the precipitation of metals from solutions.*—In apparatus for the precipitation of dissolved metallic values, the combination of a tank adapted to hold the solution to be treated, and a perforated receptacle containing scrap metal, the perforated walls of the said receptacle being composed entirely of the same material, said receptacle being partially immersed in said solution and mounted to rotate therein, whereby the solution is made to circulate through the scrap metal for the purpose set forth.

**732720—July 7, 1903.** H. DUNCAN and R. R. SHERRIFF. *Apparatus for separating liquids from solids.*—A machine for separating liquids from solids, comprising in combination a framing and gear, carrying and traversing an endless band of filter-cloth, automatic slip devices for securing the band, a vacuum-box or suction-chamber located upon the under surface of said band, and an interposed endless band of wire cloth or gauze arranged to support and travel with the filter-band.

**733739—July 14, 1903.** F. H. OFFICER, R. H. OFFICER, J. H. BURFEIND, and J. W. NEIL. *Apparatus for use in metallurgical processes.*—In an apparatus for treating ores or other materials containing gold or silver or other metals by the

cyanide process, the combination of a treating-tank, an absorption-tank containing a caustic solution, a compressor and connections as described between the compressor, treating-tank and absorption-tank whereby air or gas under pressure may be forced from the compressor through the material in the treating-tank and the gases released or freed from said material may be passed through the absorbing solution in the regenerator-tank and thence to the compressor, so as to permit the air to be used over and over and the valuable products released in the treating-tank to be recovered, as and for the purpose described.

735206—August 4, 1903. L. P. BURROWS. *Mixing and dissolving apparatus.*—A mixing and dissolving apparatus, comprising a containing vessel, a shaft in and movable relatively to said vessel, an inner and an outer set of stirring-plates carried by and arranged around and substantially parallel to said shaft, the adjacent plates of the inner and outer sets converging toward each other from their front to their rear edges, and stirring-blades secured to the rear edges of said plates and arranged in a spiral line around the shaft, the corresponding blades of the outer and inner sets being twisted in opposite directions.

735334—August 11, 1903. L. B. SKINNER. *Filter.*—A filter-bar, consisting of a body portion and separated tongues projecting laterally therefrom and recessed for the passage of filtering fluid, each tongue with a beveled end, and beveled faces on the body between the tongues.

735335—August 11, 1903. L. B. SKINNER. *Filter.*—The combination in a filter-bed, of bars having each a body portion and a perforated side flange with a beveled edge, and a beveled face constituting the bearing of the flange of the adjacent bar.

735960—August 11, 1903. G. S. FOSTER and S. S. D. STRINGER. *Metal-extracting and ore-leaching apparatus.*—The combination of a solution-supply tank, a series of intercommunicating leaching-tanks adapted to receive solution from said supply-tank, drain-pipes leading from said leaching-tanks, a launder into which said drain-pipes are arranged to discharge, and a charcoal box connected to said launder.

736036—August 11, 1903. H. L. SULMAN and H. F. KIRKPATRICK-PICARD. *Apparatus for the recovery of precious metals.*—In an apparatus for recovering precious metals, the combination of a conical vessel having an inner amalgamated copper surface, a conical body having an outer amalgamated copper surface disposed concentrically within the vessel and forming therewith a narrow interspace, a body of mercury charged with an electropositive metal in the interspace, an electrolytic vessel for charging the mercury, a mercury-pump, an inlet conduit to the top of the interspace from the electrolytic vessel, an outlet conduit for mercury from the bottom of the interspace to the pump, a conduit from the pump to the electrolytic vessel, an inlet conduit at the bottom of the vessel for the solution carrying the values, a non-return valve in said conduit, means for forcing the solution up through the interspace, and a launder at the top of the vessel to receive the discharged solution.

736078—August 11, 1903. H. T. DURANT. *Apparatus for the treatment of ores with solvents.*—A device for the treatment of ore, tailings, or other material by solvents, consisting of a tank having a conical bottom, a plug in said bottom and made conical to correspond to the angular walls thereof, a pump or forcing device discharging into the apex of the cone, and a return connection between the upper part of the tank and the suction of the pipe.

736597—August 18, 1903. C. D. GROVE. *Barrel-filter.*—In a barrel-strainer, the combination with the shell thereof of a strainer the exterior surface of which is in contact with the barrel, its inner surface being provided with suitable straining perforations in the form of slits combined with transverse grooves beneath the interior surface and establishing communication between said slits and the discharge opening.

737048—August 25, 1903. J. B. TRUITT, W. L. TRUITT, and W. O. TEMPLE. *Precipitating zinc box.*—In a precipitating zinc box, the combination of an outer impermeable box having a valved outlet in its bottom and a valved outlet above

its bottom, a launder at each outlet, and an inner removable zinc-holding box having a perforated bottom, and supported in the outer box above the bottom of the latter.

**737533—August 25, 1903. E. L. V. NAILLEN.** *Apparatus for extracting gold and other metals from ores.*—In an apparatus for extracting metals from ores, the combination of a concentrating-tank consisting of two cone-shaped sections secured together at their largest diameter by means of suitable flanges and provided with an intermediate strip secured between said flanges and projecting outwardly, a settling-tank disposed around the concentrating-tank, a perforated diaphragm placed between the concentrating- and settling-tanks and supported upon said intermediate strip, and a suitable bracket bolted to the settling-tank and adapted to form two horizontal sections within the settling-tank.

**738148—September 8, 1903. J. B. DE ALZUGARAY and W. A. MERCER.** *Apparatus for extraction of precious metals from their ores.*—Apparatus for treating ores, consisting of a closed containing vessel or vat provided with fixed internal blades or wings, a rotating hollow spindle provided with ball-bearings and having hollow blades or beaters set at an angle, means for raising and lowering the spindle in the vat, gearing for rotating the spindle, and means connected with the vat for supporting the gearing and steadying the spindle, all combined, arranged, and operating as shown and described and for the purpose set forth.

**738329—September 8, 1903. W. E. HOLDERMAN.** *Device for treating slimes.*—In a device for treating slimes having a liquid-tight case, a discharge-pipe provided with a valve in its bottom, an inclined floor in said case, spaced bars on said floor and the sides of the case, a filtering fabric covering said bars and overlapping the upper edge of the tank, a molding to hold the fabric in operative position, and pipes provided with stoppers leading from the filter out through said case.

**740193—September 29, 1903. E. D. SLOAN.** *Barrel-filter.*—In a barrel-filter, the combination with the barrel of a partial lining of porous filter-blocks fitting closely together and having grooves formed on their under sides which interconnect from block to block and form drain channels; means for sealing said draining channels from the inner space of the barrel, and a discharge port leading from the drains out of the barrel.

**741189—October 13, 1903. H. H. THOMPSON.** *Apparatus for extracting precious metals.*—An apparatus for extracting precious metals, comprising a receptacle provided with an outlet, a series of bodily movable and loosely mounted agitating arms gradually decreasing in length and adapted to be retained in their operative position when rotated in one direction and to assume an inoperative position when moved in an opposite direction, a rotatable means for suspending said arms within said receptacle, said rotatable means and arms bodily movable, a series of screened nozzles communicating with said receptacle, means for supplying a cyanide solution, compressed air and water to each of said nozzles either separately or in any preferred combination, operating means for said rotatable means, and means communicating with said supply means and the said outlet for exhausting the solution from said receptacle.

**741402—October 13, 1903. W. E. HOLDERMAN.** *Leaching-tank.*—In a filtering-tank having vertical slats covered with a filtering fabric, a filtering partition extended across said tank, a trough in its bottom for the filtrate, and an orifice through the filtering fabric of said tank into which the filtrate from said trough is discharged.

**741499—October 13, 1903. A. E. JOHNSON.** *Barrel-filter.*—In a barrel-filter, the combination with a suitable barrel or cylinder, of a filter having a perforated bottom, side walls extending below the bottom and engaging the barrel on the inside, filtering material resting on the bottom and confined by the side walls, a top perforated plate, and suitable means for securing the filter in place, a channel being formed underneath the bottom of the filter to receive the filtered liquid, the barrel being provided with a valved outlet in communication with the said channel.

**743550—November 10, 1903.** J. A. OGDEN. *Process of extracting metals from cyanide solutions.*—The process of treating gold, silver, or other metals from a cyanide or primary solution, consisting in mixing in a receptacle a given quantity of said primary solution with a given quantity of a secondary solution having a metal base and capable of liberating the metals in said primary solution; leaving said mixture in said vessel until said liberation is partially effected, then passing said mixture into a second receptacle and agitated therein so as to produce a complete commingling of said solutions, from thence running the mixed solution into a settling-tank and allowing it to settle, drawing off the clear solution, and then drying the precipitation and pressing and melting it into bullion.

**743551—November 10, 1903.** J. A. OGDEN. *Apparatus for extracting precious metals from cyanide solutions.*—An apparatus for the purpose set forth, consisting of primary and secondary solution-tanks, each provided with discharge-pipes with controlling-cocks, and measuring-glasses; a mixing vessel adapted to receive the flow from said measuring-glasses; a barrel with rotatable blades therein and having a glass gauge on the outer face thereof, and a settling-tank adapted to receive the discharge from said barrel.

**745472—December 1, 1903.** W. H. ADAMS, JR. *Apparatus for treating ores.*—The combination of a tank, a box, a pipe at the top of the tank connecting the same with the box, a pump connected with the box, and nozzles connected with the pump and arranged to discharge liquid into the tank at intervals tangentially in an approximately horizontal plane.

**746867—December 15, 1903.** DE W. C. MOSHER. *Chlorination barrel.*—A chlorinating barrel provided with a resistant lining and with an arched channeled rib extending longitudinally, secured to said lining and having perforations between the interior of the rib and barrel, and a discharge opening communicating with the interior of the rib.

**748088—December 29, 1903.** G. MOORE. *Filtering system.*—In a filtering system, the combination with a tank for containing the material to be filtered and a cleansing-fluid tank, of a filter, means for introducing and removing the same into and from each of said tanks alternately, means for drawing the contents of said tanks through the filter, and means for cleansing the filter.

**748217—December 29, 1903.** C. H. RIDER. *Apparatus for dissolving organic or inorganic substances.*—A device consisting of an acid-tank, a water-tank, an upper series of tanks connected with the acid-tank and the water-tank and to each other, a lower series of tanks adapted to receive the substance to be treated, connected to the upper series of tanks and to the water-tank and to each other; a retort, means for heating the retort, a pipe passing from the retort through the lower series of tanks, and a condenser into which the last-named pipe extends, substantially as and for the purposes specified.

**748462—December 29, 1903.** W. J. ARMBRUSTER. *Chlorination barrel.*—A chlorination barrel having a pulp-chamber and a chlorine generating compartment rotatable therewith, a wall separating the pulp-chamber from the compartment, said wall having an unobstructed opening disposed about the axis of rotation of the barrel for freely permitting the discharge of the chlorine above the surface of the pulp in the pulp-chamber.

## CLASS 75—METALLURGY.

### SUBCLASS 185—CYANIDES.

**323222—July 28, 1885.** J. W. SIMPSON. *Process of extracting gold, silver, and copper from their ores.*—The ore is crushed to a powder, treated with a solution produced by dissolving 1 pound of cyanide of potassium, 1 ounce of carbonate of ammonia, and  $\frac{1}{2}$  ounce of chloride of sodium in 16 quarts of water when the ore contains gold and copper only; but when it is rich in silver the quantity of chloride of sodium employed is increased. After thorough agitation of the ore in the solution the mixture is allowed to stand until the solution has become

clear, when the dissolved metals are precipitated out by means of a plate of zinc suspended in the liquid. The metal is precipitated upon the zinc and can be removed by scraping or by dissolving the zinc in sulphuric or hydrochloric acid.

403202—May 14, 1889. J. S. MACARTHUR, R. W. and WM. FORREST. *Process of obtaining gold and silver from ores.*—The invention consists in subjecting finely-powdered argentiferous ores to the action of a solution containing a small quantity of a cyanide, the cyanide contents of the latter being proportioned to the quantity of gold or silver, or both, found, by assaying or otherwise, to be in the ore. Any cyanide soluble in water may be used, but in all cases the solution must be extremely dilute, since such a solution has a selective action in dissolving gold or silver in preference to the baser metals. The claim covers the use "of a cyanide solution containing cyanogen in the proportion not exceeding 8 parts of cyanogen to 1000 parts of water."

418137—December 24, 1889. J. S. MACARTHUR, R. W. and WM. FORREST. *Process of separating gold and silver from ore.*—This invention has for its object the preventing of loss of cyanide in the care of weathered ores by first neutralizing the ore with an alkali or alkaline earth and then leaching such prepared charge with a cyanide solution. Further, the precious metal thus dissolved in the cyanide solution is precipitated out by passage through a sponge of zinc composed of fine threads or filaments of zinc formed by cutting shavings with a turning tool from a series of zinc disks held in a lathe, or by passing molten zinc at a temperature just above the melting-point through a fine sieve and allowing it to fall into water.

432577—September 13, 1892. E. D. KENDALL. *Composition of matter for the extraction of gold and silver from ores.*—Consists in extracting gold and silver from minerals, "tailings," and other matters containing one or both of these metals by an aqueous solution of one or more soluble ferricyanides and one or more soluble cyanides prepared by dissolving a ferrocyanide in one portion of water and a cyanide in another portion and mixing the two solutions, or by adding either salt in solid form to the solution of the other.

492221—February 21, 1893. C. MOLDENHAUER. *Extracting gold from its ores.*—Consists in subjecting gold ores to the solvent action of cyanide of potassium in the presence of ferricyanide of potassium.

494064—March 21, 1893. W. A. G. BIRKIN. *Process of and solvent for separating precious metals from their ores.*—Covers the art of separating metals from their ores by subjecting the suitable comminuted ore to the action of a menstruum composed of potassium cyanide, potassium ferricyanide, and peroxide of hydrogen in water, and separating the values from this solution by precipitation, deposition, or electrolysis.

498950—May 9, 1893. H. PARKES and J. C. MONTGOMERIE. *Process of extracting gold or silver.*—Claims a process for extracting gold and silver from ores or compounds by an interrupted operation, consisting of treating the ore with cyanide of potassium in the presence of oxygen under pressure with agitation, the ore being subsequently filtered and washed and the precious metals recovered from the liquor by precipitation or other known means.

514157—February 6, 1894. W. P. MILLER. *Process of recovering precious metals.*—Has for its object the preservation of the cyanide solution, and consists in the treatment of the ore with the cyanide solution in air-tight vessels not only during the process of solution, but during the filtration and up to the time of the precipitation of the precious metals from the filtered solution.

522739—July 10, 1894. C. MOLDENHAUER. *Process of precipitating gold or other precious metals from their solutions.*—Dissolves gold and other precious metals from their ores by means of acid-cyanide solutions, which consist in treating the solution with aluminum, so as to precipitate the gold from the solution, and then add a free alkali or alkaline earth for a regenerating solution.

524601—August 14, 1894. J. C. MONTGOMERIE. *Process of extracting gold or silver from ores.*—Sodium oxide (caustic soda) or other suitable oxide of the alkalies is added to the cyanide solution before mixing the same with the ore.

After the precious metals have been dissolved in the solution and the liquid filtered off and the precious metals precipitated out, the remaining solution is tested to determine the quantities of potassium and sodium oxide still remaining in it, and any deficiency is supplied or the solution fortified by the addition of the necessary quantity of these agents, so as to restore the solvent solution to its original character and strength.

**524690—August 14, 1894.** E. D. KENDALL. *Method of treating gold or silver ores.*—Covers the treating of gold or silver ores with a composition of matter consisting of sodium dioxide and a suitable cyanide in solution.

**532238—January 8, 1895.** C. MOLDENHAUER. *Method of precipitating precious metals from solutions.*—Consists in subjecting the ores to the action of an acid-cyanide solution so as to dissolve the gold or other precious metal contained in them, then adding aluminum so as to precipitate the gold or other metal from the solution, and then regenerating the cyanide solution by means of a free alkali or alkaline earth.

**532895—January 22, 1895.** J. C. MONTGOMERIE. *Process of extracting gold or silver from ores.*—Consists in adding an oxide or one of the alkaline bases to a cyanide solution, then mixing with the ore or compound the solution thus rendered alkaline, then conducting the process under pressure of oxygen, and afterwards separating from the ore the liquid containing the gold and silver in solution, then treating that liquid in any approved way for the recovery of the precious metal.

**538951—May 7, 1895.** S. C. CLARK. *Process of treating refractory ores.*—Claims the process of treating a refractory ore, consisting essentially in boiling the ore in water containing from 10 to 15 pounds of cyanide of potassium to each ton of ore for about one hour or for a sufficient length of time to enable the cyanide of potassium to dissolve the chloride, sulphide, or bromide in the ore, then allowing the solution to settle and finally evaporating the clear liquid so as to obtain a residue containing metal.

**540359—June 4, 1895.** G. KENNAN. *Process of and apparatus for treating ores.*—Claims the process of treating the ores of gold and silver, consisting in subjecting the same to the action of cyanide of potassium, agitating the same for a short period of time, discontinuing the agitation, and bringing air in contact therewith, the oxygen thereof increasing the action of the cyanide, continuing the agitation for a few minutes, until every particle of ore has been brought in contact with the cyanide solution in the presence of atmospheric air, and withdrawing the solution from the remaining pulp or ore.

**541333—June 18, 1895.** F. RINDER. *Process of separating gold and silver.*—Consists in the treatment of cyanide solutions containing gold and silver with sulphide of iron to precipitate the silver and then with chloride of zinc to precipitate the gold.

**543543—July 30, 1895.** M. E. WALDSTEIN. *Process of extracting gold or silver from ores.*—Consists in subjecting the ores to the action of cyanide of potassium, adding to the material during this action a salt or salts (such as binoxide of barium) decomposable by an acid and yielding oxygen, and sufficient acid to decompose this salt or salts, and subsequently adding an excessive acid to decompose the soluble cyanide and finally separating the precious metals as sulphides by precipitation with sulphureted hydrogen or by a soluble sulphide.

**543782—July 30, 1895.** M. CRAWFORD. *Process of extracting precious metals from their ores.*—Consists first in lixiviating the ores of the precious metals with a cyanide solution to which has been added a substantially neutral substance which contains a permanent excess of oxygen; second, in subjecting the gangue and accompanying cyanide solution to an amalgamating process; and, thirdly, in withdrawing the solution from the tailings, and extracting the precious metals therefrom. The neutral substance containing a permanent excess of oxygen may be prepared by mixing peroxide of sodium with dilute sulphuric acid and neutralizing with silicate of soda.

**543676—July 30, 1895.** M. CRAWFORD. *Process of extracting precious metals from their ores.*—Consists in, first, lixiviating the ore with a cyanide solution to

which has been added a small quantity of a substance prepared by agitating ether with binoxide of barium and adding thereto small quantities of very dilute hydrochloric acid, and neutralizing by silicate of soda, and, second, separating the precious metal from this solution in which the ore has been lixiviated.

545852—September 3, 1895. P. DE WILDE. *Method of extracting gold*.—The precipitation of gold in the form of a mixture of aurous cyanide and cuprous cyanide by acidulating a cyanide solution containing the gold with an acid sulphurous compound and afterwards adding a solution of copper salt. Also, specifications provide for the dissolving of gold by the use of a weak solution of potassium or sodium cyanide which has been in contact with the minimum or protoxide of lead, and for the recovery and utilization of the spent cyanide by its conversion to Prussian blue.

547790—October 15, 1895. J. J. HOOD. *Extracting metals*.—The method for the extraction of precious metals from their ores, which consists in treating the ore with a solution containing both a cyanide of potassium or sodium and a salt or compound of a baser metal in the proportion of one part at least of the former to two parts of the latter; the metallic base of the solution being displaced by the precious metal, the former being precipitated. The gold is then precipitated out by a copper-zinc couple. By "baser metal" is meant mercury, lead, and such other metals as are displaced by metallic gold from their solutions in alkaline cyanides. A mixture that answers well consists of two parts, by weight, of cyanide of potassium (or its equivalent of cyanide of sodium), one part of mercuric chloride or its equivalent of sulphate or other mercury salt, and from one-half to two parts of caustic soda.

549736—November 12, 1895. J. C. MONTGOMERIE. *Extraction of gold and silver from ores*.—The improved process of extracting gold and silver from ores or compounds containing the same, consisting in treating the ore in a vessel containing water with a cyanide, an alkaline oxide, a nitrate, and an oxidizing agent. Sodium dioxide may be taken as a representative of the alkaline oxide and aid under pressure as an oxidizing agent, as set forth in this claim.

555463—February 25, 1896.—J. S. MACARTHUR and C. J. ELLIS. *Process of extracting gold and silver from ores*.—Consists in subjecting the ore to the action of a cyanide solution and precipitating, by means of a metallic compound capable of combining with sulphur any sulphur which may become soluble in the solution and thereby rendering it inert. Salts or compounds of lead, manganese, zinc, mercury, and iron are types of the metallic compound employed. By means of a salt of lead any copper present in the cyanide solution may be precipitated out.

555483—February 25, 1896. T. L. WISWALL and J. B. FRANK. *Process of recovering precious metals from solutions*.—The process of extracting precious metals from solutions by causing said solutions to flow through a precipitating alloy, subdivided into a mass of hardened filaments, and composed of zinc, lead, and one or more other metals which impart to said filaments a tensile strength sufficient to withstand the compression of the flowing solution, such as arsenic, antimony, cadmium, or bismuth, and in which alloy there is present not more than 97 per cent. of zinc.

576173—February 2, 1897. H. L. SULMAN. *Process of precipitating precious metals from their solutions*.—Consists in purifying zinc fumes or dust of oxides by intimately mixing with the same an ammoniacal substance, and then mixing a quantity of said fumes or dust so purified with the solution. The apparatus by which to perform the process and for the treatment of the ores is also claimed.

578089—March 2, 1897. J. F. WEBB. *Process of extracting gold and silver from ores*.—The process or method for the extraction of gold and silver from their crushed ores, consisting in saturating the ores in a solvent solution of potassium cyanide, then applying a current of compressed air from beneath and maintaining the same throughout the leaching process, then shutting off the current, then applying a current of compressed air on top of the solution after the ore-containing vat has been closed at top and a drain at the bottom has been opened, and maintaining the same until the solution has been driven out of the ore, then shutting off the current of air, then admitting water to the vat, then introducing a

compressed-air current at the bottom of the vat, and finally introducing a current of compressed air on top after the vat has been again closed at top and a drain opened at bottom.

578178—March 2, 1897. D. WHITE and T. M. SIMPSON. *Process of and apparatus for extracting precious metals from slimes, etc.*—In the extracting of precious metals from slimes and other auriferous and argentiferous materials, the process which consists in mixing the said material with a cyanide solution in a closed vessel, then agitating the mixture by passing a gas under pressure through the same, then passing gas under pressure, together with the gases arising from the action of the cyanide solution in the said material, through another quantity of said material and cyanide solution in a closed vessel, then conveying the gases back to the source of compression and drawing off the solution, containing the precious metal and extracting said metal. The apparatus for accomplishing this purpose is also claimed.

578340—March 9, 1897. W. A. KONEMAN. *Process of extracting precious metals from their ores.*—The process of extracting precious metal from the ore containing it, which consists in wetting the ore, in a pulverized condition, with just sufficient cyanogen-containing solution to moisten the ore and reduce the mass to the condition of mud, maintaining the saturated ore in a quiescent state for a prolonged period of time, then diluting the mass and subjecting it to agitation for a suitable period of time, separating the resultant solution from the ore by filtration, and finally precipitating the precious metal from said solution.

578341—March 9, 1897. W. A. KONEMAN. *Process of recovering precious metals from cyanide solutions containing them.*—The process of recovering, by precipitation, the precious metal or metals contained in a cyanogen-containing solution, which consists in subjecting said solution to contact with an alloy composed of lead and zinc, and in which lead is the preponderating metal in weight, or with an alloy composed of lead, zinc, and aluminum.

580683—April 13, 1897. C. W. H. GÜPNER and H. L. DIEHL. *Recovery of gold and silver from their solutions.*—The process for the precipitation of gold and silver from their cyanide solutions, which consists in adding to said solutions a considerable quantity of cuprous cyanide, then adding an acid to effect precipitation, dissolving the latter by a fresh quantity of the cyanide solution obtained by leaching, and then adding acid to effect successive precipitations from said solution.

580948—April 20, 1897. J. C. MONTGOMERIE. *Process of treating cyanide solutions.*—The process for the extraction of the precious metals from cyanide solutions, which consists in filtering the solution through a charcoal filter, heating the filtering material on the same becoming surcharged with cyanogen or its compounds, condensing the resultant gases and obtaining ammonium cyanide and other ammonium salts in solution, applying the regenerated charcoal (still containing the precious metals) in the filtration of a further charge or charges of the solution, and ultimately recovering from the charcoal the precious metals accumulated therein.

587179—July 27, 1897. J. H. BURFEIND. *Treatment of gold and silver ores.*—As an improvement in the extracting of precious metals from their ores, the treatment of the cyanide product or precipitate containing said metals, preparatory to melting the said product with sulphurous acid.

591753—October 12, 1897. E. J. FRASER. *Process of obtaining precious metals by solution.*—The process of treating gold and silver ores by solution, which consists in converting the metal bases of dioxides of the alkaline metals into sulphates, by the addition of sulphuric acid, so as to produce hydrogen dioxide, preventing the decomposition of the hydrogen dioxide by an excess of acid, separating the solution from the metallic sulphate, mixing the solution with a solution of cyanide of potassium and lime in the presence of a precious metal, and leaching the liquid holding the precious metal.

592153—October 19, 1897. J. S. MACARTHUR. *Precipitating precious metals from solutions.*—The process of precipitating a precious metal from a cyanide solution, which consists in subjecting said solution containing a base metal to the action of a precipitant protected by a metal inert in said solution. Such a



precipitant is found in zinc, mercury, or copper protected by lead. When copper is present in the cyanide solution, this copper is removed by the precipitant prior to the removal of the precious metal.

601801—March 22, 1898. S. NEWHOUSE, A. J. BETTLES, and T. WEIR. *Method or process of extracting precious metals from their ores.*—A method or process for the extraction of the precious metals from their ores, said method or process consisting, first, in neutralizing the acidity of the ore where this condition exists; second, in placing the ore in a suitable solution of cyanide of potassium and subjecting the mass to agitation; third, in adding a quantity of zinc to the mixture of ore and cyanide and subjecting the mass to further agitation; and, fourth, in adding quicksilver or mercury charged with sodium amalgam, and finally agitating the entire mass for purposes of amalgamation.

607719—July 19, 1898. M. E. WALDSTEIN. *Process of recovering precious metals from their solutions.*—The process for extracting and recovering precious metals from their ores, which consists essentially of the following steps: First, subjecting the ore in a powdered state to the action of an aqueous solution of a cyanide; second, supplying to the solution charged with the precious metals that quantity of zinc dust determined to be exactly sufficient to precipitate said metals; third, agitating said solution and said zinc dust until said metals are precipitated and said zinc dust is absorbed; fourth, recovering the precious metals from the valuable precipitate of the preceding step by filtration, or other process.

610616—September 13, 1898. H. L. SULMAN and F. L. TEED. *Extraction of precious metals from their ores.*—The essence of this invention consists in the employment of haloid compounds of cyanogen in combination with free cyanide of potassium or other suitable cyanide of the alkalies or alkaline earths as a solvent for precious metals in their ores, examples of such haloid compounds of cyanogen being found in cyanogen chloride, or bromide or iodide.

620100—February 28, 1899. W. A. CALDECOTT. *Method of extracting gold from cyanide.*—An improved method for the precipitation of gold from gold-bearing cyanide solutions by passing such solutions over zinc shavings previously treated with a soluble salt of mercury, such as perchloride of mercury ( $\text{HgCl}_2$ ).

624040—May 2, 1899. C. B. JACOBS. *Process of reducing metals from their solutions.*—The process of reducing metals from their solutions, consisting in subjecting them to the action of gaseous phosphide of hydrogen in the presence of an alkaline material, thereby precipitating the noble metals in a metallic state and the base metals as phosphides, and then separating the latter from the noble metals.

625564—May 23, 1899. E. D. KENDALL. *Process of treating gold or silver ores and composition of matter for same purpose.*—A composition of matter to be used for extracting precious metals from ores, tailings, or other bodies, consisting of a suitable thiocyanate and a suitable ferrocyanide in watery solution.

625565—May 23, 1899. E. D. KENDALL. *Process of treating gold or silver ores and composition of matter for same purpose.*—A composition of matter to be used for the extraction of precious metals from ores, tailings, or other bodies, consisting of a suitable thiocyanate and hydrogen dioxide in watery solution.

629905—August 1, 1899. J. J. HOOD. *Process of extracting gold or silver.*—The process of extracting gold, silver, and mercury from solutions by bringing the solutions into contact with an alloy of zinc, antimony, and mercury, from time to time distilling off mercury from the alloy, and finally recovering the gold and silver from it. The precipitant used consists of an alloy of about one hundred parts of zinc, five parts of antimony, and twenty parts of mercury.

630982—August 15, 1899. W. KEMMIS-BETTY and B. SEARLE. *Process of recovering gold from pulp, slimes, or similar substances.*—The process of extracting gold from ores, which consists of the following steps: First, dissolving the gold in the pulp in a weak solution of cyanide of potassium; second, adding a stronger solution of cyanide of potassium to the gold-bearing solution in the proportions

specified; third, immediately after so strengthening the solution, passing the same through a body of zinc shavings coated with lead.

635199—October 17, 1899. J. SMITH. *Process of treating gold or silver ores.*—The process for treating gold and silver ores, tailings, slimes, and like materials containing precious metals, which consists in mixing the material to be treated with caustic lime, saturating or covering the mixture entirely with water and keeping it thus until all the acid present has combined with the lime, drying the material, exposing it to the action of atmospheric air, and treating it with a cyanide.

636114—October 31, 1899. J. S. CAIN, A. SODERLING, and S. M. MACKNIGHT. *Preliminary treatment of ores or tailings before cyaniding.*—The method or process of treating ores containing the precious metals, which consists in first leaching said ores or tailings in a weak solution of nitric acid, or of nitric and sulphuric acids, subsequently leaching the same in an alkaline solution, and finally leaching the same in a cyanide solution.

636288—November 7, 1899. H. DE RAASLOFF. *Process of extracting precious metals from ores.*—The improvement in the process of separating precious metals from their ores, consisting in mixing with the ore a solution consisting of a base and a solvent for precious metals, which solvent is capable of being separated from the said base by oxygen, and adding liquid air to the ore and solution, or by evaporating the nitrogen from liquid air, and adding the oxygen which remains to the mixed ore and solution.

638372—December 5, 1899. M. B. ZERENER. *Precipitation of precious metals from their cyanide solutions.*—The process of precipitating gold and silver from cyanide solutions by causing the solution to move in one direction, and during such movement passing through it, in the opposite direction and in the form of a spray, or a number of fine streams or films, mercury charged with alkali metal.

641818—January 23, 1900. C. WHITEHEAD. *Process of extracting gold from ores.*—The process of extracting gold from ores in which the particles of free gold are enveloped in a compound of a base metal having the following characteristics, to wit: non-siliceous, oxidized, practically impervious to a solvent solution, such as one of cyanide, not readily removable by washing with water, and insoluble in water, but soluble in dilute acids, consisting in first subjecting the crushed ore to the action of heat sufficient to convert the coating into a porous condition and afterwards treating the ore with a cyanide solution.

642767—February 6, 1900. G. THURNAUER. *Process of separating precious metals from their mixtures with zinc.*—The process of treating the mixture of zinc and precious metals resulting from the treatment of cyanide solutions of the precious metals by zinc, which consists in subjecting said mixture to the action of a solution containing lead and then to the action of acid, whereby the zinc is dissolved and the precious metals remain in admixture with metallic lead.

648006—March 27, 1900. J. C. MONTGOMERIE and H. PARKES. *Treatment of gold and silver ores, etc.*—In the extraction of gold and silver from ores or compounds containing the same, the process consisting in treating the ore or compound with a cyanide of an alkali metal, caustic alkali, and barium dioxide, in conjunction with ammonium sulphate.

646808—April 3, 1900. T. CRUSE. *Method of extracting gold and silver from their ores.*—The process of recovering precious metals from their ores, which consists in first heating the ore pulp to the boiling-point, adding cyanide of potassium to the hot mass, permitting the mass to gradually cool, and while it is cooling adding to the mass the following: Bluestone, iron sulphate, sulphuric acid, and quick-silver.

649628—May 15, 1900. W. A. CALDECOTT. *Extraction of gold or other precious metals from slimes.*—The method of extracting precious metals from finely divided materials, such as slimes, containing reducing substances, such as ferrous sulphide or hydrate, which consists in rendering the material alkaline, then forcing air into the pulp until the ferrous compounds are converted into ferric hydrate, then adding cyanide and continuing aeration and agitation until the precious metals are dissolved.

651509—June 12, 1900. F. W. MARTINO and F. STUBBS. *Precipitation of precious metals from cyanide solutions.*—A process for the precipitation of the precious metals from their aqueous cyanide solutions, consisting in passing acetylene and atmospheric air through such solutions, or by adding calcium carbide to them, and precipitating the metals in a metallic state.

651510—June 12, 1900. F. W. MARTINO and F. STUBBS. *Treatment of ores and precipitation of precious metals from their cyanide solutions.*—A process for the precipitation of precious metals from their aqueous-cyanide solutions, consisting in treating such solutions with a hydrocarbon gas, produced when a metallic carbide is decomposed by water, and capable of precipitating the metals in a metallic state. Aluminum carbide is given as an example of such a metallic carbide. The use of methane as a precipitant is also claimed.

657181—September 4, 1900. H. DE RAASLOFF. *Process of separating precious metals from their ores.*—The continuous process of treating ores of precious metals, consisting in mixing the finely divided ore with a suitable solvent for the precious metals, inducing the mixture to flow continuously from and back to the point of admixture, while so flowing introducing liquid oxygen or liquefied air into the mixture, then causing the mixture to flow with sudden variations of velocity to agitate it, then separating the solution from the base earthy mineral matter, and sending it continuously through an electrodepositing bath, where the precious metal is deposited, and thus in continuous ordered succession.

656395—August 21, 1900. E. H. DICKIE. *Process of leaching ores or tailings.*—The improvement in the process of leaching ores or tailings with a solution which dissolves the precious metals, which consists in adding to the solution an agent composed of an acetate of an alkali metal or of alkali-earth metals which is capable of readily uniting with and forming acetates of the base metals, and which has little or no affinity for the precious metals, thereby enabling the solvent to act directly upon the latter, and then leaching the ores. Calcium acetate is cited as an example of an acetate of an alkali-earth metal.

664060—December 18, 1900. J. P. SCHUCH, Jr. *Process of extracting precious metals from their ores.*—A method of extracting precious metals from their ores, which consists in combining the crushed ore with a cyanide solution while both are in a warm condition, mechanically mixing the ore and solution by agitation simultaneously with the commingling thereof, charging the mixture during the agitation with hot air, and finally separating the ore and slush or pulp from the metal in solution.

665105—January 1, 1901. J. C. KESSLER. *Process of extracting gold and silver from ores.*—The process of separating precious metals from auriferous and argentiferous ores, consisting, first, in subjecting the ores to the action of an aqueous solution, consisting of cyanide of alkali metal, yellow prussiate of potassium, and permanganate of an alkali metal in substantially the proportions of water, one thousand (1000) parts; yellow prussiate of potassium, two and one-half (2.5) parts; cyanide of alkali, two and one-half (2.5) parts; permanganate of potassium, one-tenth (0.1) part, until the gold and silver contained in such ores are dissolved; second, separating the metals from their solution by the application of a soluble lead salt, by which the cyanide solution is decomposed and a non-soluble cyanide of lead is formed, at the same time a non-soluble cyanide of gold or silver is precipitated; third, by the application, to the sediment thus precipitated, of sodium amalgam, whereby a gold, silver, and lead amalgam is produced and at the same time a concentrated solution of cyanide and ferrocyanide of sodium is regenerated; and, fourth, diluting the concentrated cyanide solution with a quantity of water and regenerating and reenergizing the aqueous solution for reuse by the addition of permanganate of alkali.

671704—April 9, 1901. E. D. KENDALL. *Process of treating ores containing silver or silver and gold.*—The process of treating ores or other bodies for the extraction of precious metals, which consists in treating them with a suitable chemical solution containing a thiocyanate and a cyanide, capable of dissolving silver and gold, and in then treating the so-dissolved silver by a suitable sulphide, such as potassium sulphide, and in so regulating the amount of the sulphide to the silver

as that they shall substantially equalize each other in separating the sulphur sulphide and in returning the thiocyanate and cyanide into subsequent operations for further treatment of the ore.

673425—May 7, 1901. G. A. DUNCAN and F. H. BEACH. *Method of treating precious metal-bearing ores.*—The method of treatment of precious metal-bearing ores to cause the precious metal to be dissolved from the ore, and the resulting metal-bearing liquor and impoverished ore to be separated from each other, which consists in the following steps: First, maintaining a substantially continuous supply stream of mingled comminuted ore and solvent liquor; second, mechanically dispersing such mingled ore and liquor into the air, in a direction transverse to the onward movement of the stream, without separating the ore from the liquor; third, delivering the resultant stream of mingled metal-bearing liquor and impoverished ore and receiving the same in mingled condition and carrying it onward; fourth, sucking the liquor from the tailings; fifth, delivering water to the impoverished tailings remaining, and subsequently sucking such wash-water therefrom; sixth, delivering such impoverished ore or tailings after the application of such suction.

682612—September 17, 1901. E. L. GODBE. *Method of leaching ores.*—The method of leaching ores, which consists in disposing moistened ore in superimposed strata within a containing receptacle by a continuous mechanical agitation in the lower portion of the latter to form a lower thoroughly agitated stratum of heavier portions of the ore, a stratum of lighter portions or particles next above which are agitated to a less degree, a stratum of slimes and other lighter particles next above which remain substantially immobile, and a top covering of a clear supernatant solution, introducing the ore below the upper surface of said latter solution, overflowing and carrying off the clear solution, replacing water in the charge by a cyanide of potassium solution introduced at the bottom of the receptacle below the lower heavier stratum and causing it to percolate upwardly through the strata above, increasing the agitation during the introduction of said cyanide solution, carrying off the metal-bearing cyanide solution which overflows from the top of the charge and precipitating the said overflow metal-bearing solution after it leaves the receptacle.

689190—December 17, 1901. B. HUNT. *Process of precipitating and recovering precious metals from their solutions.*—The process of precipitating precious metals, consisting of adding to the pulp a cyanide solution and agitating the same until the metal is extracted; then adding to the pulp, while continuing the agitation thereof, powdered metallic aluminum whereby the precious metal is precipitated, but in suspension in the pulp; then adding mercury and continuing the agitation until the metal is in the form of an amalgam, and finally recovering the precious metal by treating the amalgam.

692634—February 4, 1902. H. DAVIS. *Process of extracting precious metals from their ores.*—A process for the extraction of the precious and other metals from ore, ore pulp, sands, slimes, tailings, mineral-bearing earths or other substances containing these metals, which consists in introducing chlorine gas into the ore and afterwards wholly or partially removing the excess of chlorine by forcing air into the material and afterwards treating with a cyanide solution to dissolve the chlorides.

694521—March 4, 1902. B. W. BEGEER. *Cyanide process of extracting precious metals from ores.*—The process of treating material containing the precious metals, consisting in setting in motion in an endless path a solution of cyanide of potassium, introducing oxygen to the moving liquid, and finally subjecting the metal-bearing material to the action of said solution.

696274—March 25, 1902. E. SCHILZ. *Cyanide process of extracting precious metals from their ores.*—An improved process in the art of extracting precious metals from their ores, said process consisting in thoroughly and intimately mixing peroxide of barium ( $\text{BaO}_2$ ) with precious metal-bearing material, and then subjecting the same to treatment with an alkaline-cyanide solution.

701002—May 27, 1902. J. B. DE ALZUGARAY. *Method of extracting precious metals from their ores.*—The process for treating ores containing precious metal

and consisting in adding the crushed ore to a solution of sodium chloride, sodium carbonate, and potassium cyanide, then forcing through the mass a gaseous mixture of bromine and air and recovering the precious metals from the solution by any known means, such as electrolysis.

702305—June 10, 1902. E. D. KENDALL. *Process of extracting precious metals from their ores.*—The process of treating ores carrying precious metals, which consists in treating such ore with a lixiviating solution, consisting of a cyanide, potassium percarbonate, and water, and finally extracting the precious metal from such lixivium.

705698—July 29, 1902. R. H. OFFICER, J. W. NEIL, J. H. BURFEIND, and F. H. OFFICER. *Cyanide process of working gold, silver, or other ores.*—The improvement in treating ores by the cyanide process, consisting in agitating the pulp containing the cyanide solution by a suitable gas under pressure, passing the gas and the hydrocyanic-acid gas liberated from the solution through a regenerating solution, and using the gas after passing through said regenerating solution to agitate a fresh quantity of pulp.

706303—August 5, 1902. L. B. DARLING. *Process of extracting precious metals from ores.*—The process of extracting precious metals from finely divided materials or ores, which consists in spreading a comparatively thin layer of the material over a substantially flat and large working surface provided with drainage ducts or channels; then covering said material with suitable metal-dissolving or cyanide solution; then passing a heavy roll back and forth over the charge of material, etc., thereby at the same time thoroughly agitating or stirring the charge and forcing some of the solution into the drainage ducts; then discharging said solution into the sump, and finally precipitating the precious metal from the solution.

707926—August 26, 1902. W. HILT and C. E. LANE. *Process of extracting precious metals.*—The process of extracting precious metals from solutions thereof, which consists in producing cyanide solutions of said metals, vaporizing metallic zinc by means of heat, and conducting the vapor thus formed to a point beneath the surfaces of said solutions, thus producing finely divided zinc, which replaces the precious metals and thereby causes their precipitation.

708504—September 2, 1902. H. L. SULMAN and H. F. KIRKPATRICK-PICARD. *Treatment of ore slimes.*—The process of treating ore slimes, which consists in separating, by means of a centrifugal machine, the ore slimes from the residual water with which they are mixed by adding a little lime to the charge, removing the bulk of the water, thereafter introducing into the machine an amount of leaching solution of a volume equal to that of the remaining quantity of adhering moisture and introduced into the slimes by centrifugal action, and replacing the moisture by the added leaching solution.

710496—October 7, 1902. S. T. MUFFLY. *Process of treating ores.*—The process of treating ores, which consists in injecting into said ores, as they are agitated and elevated and allowed to fall by gravity in a closed chamber, a chemical solution in the form of a spray, together with hot air under pressure, and allowing the elements and fumes freed by this operation to escape from said chamber.

718633—January 20, 1903. T. B. JOSEPH. *Gold-extracting process.*—The process of extracting gold or silver from ore containing the same, when in a suitable condition, which consists in subjecting the said ore to the leaching action of a solution of water, cyanide of potassium, hydrate of calcium, and carbonic-acid gas, and introducing an oxidizing agent into the solution, and subsequently precipitating the gold from this solution.

719274—January 27, 1903. Z. B. STUART. *Process of extracting metals from ores.*—The process of extracting precious metals from ores, consisting in agitating the pulp together with cyanide, water, and air by ebullition in one vessel, causing the mixture to assume an even consistency throughout, and passing the mixture through a mechanical agitator and combining therein a relatively smaller quantity of mixture with a relatively larger quantity of air and there forcing the

pulp, cyanide, water, and air into intimate contact, and circulating the mixture through the two vessels.

**722455—March 10, 1903.** AUGUST PRISTER *Process of precipitating gold from cyanide solutions.*—The process for the precipitation of gold or other precious metals from cyanide solutions, such as potassium cyanide, sodium cyanide, and bromine cyanide, which consists in acidifying the solution, adding a solution containing salts of mercury and copper, and then adding a solution containing zinc salts and a small percentage of a potassium ferrocyanide, or a small quantity of the cyanide solution discharged from the ordinary zinc-precipitation boxes.

**722762—March 17, 1903.** J. P. SCHUCH, Jr. *Process of separating precious metals from solvent solutions.*—The process of separating precious metals from their solvent solutions, which consists, first, in passing the solution through crushed limestone or phonolite to neutralize any free acid, then through zinc, wood ashes, asbestos wool or its equivalent, and charcoal or coke, to neutralize any free soda or carbonates, then through zinc shavings to precipitate the precious metals, then through charcoal to filter the solution and effect retention of a percentage of the precious metals, then through limestone or crushed phonolite to effect precipitation of zinc contained in the solution, and then alternately through zinc, charcoal, or coke and zinc to effect complete separation of the precious metals and thorough filtration of the solution.

**725895—April 21, 1903.** M. V. USLAR and G. ERLWEIN. *Process of extracting gold.*—The process for extracting gold from auriferous ores, which consists in lixiviating the ores with a solution of potassium cyanide, rhodanides, hyposulphites, and sodium chloride.

**726294—April 28, 1903.** F. J. HOYT. *Method of extracting gold from ores.*—The method of milling gold ore, consisting of the following steps: First, pulverizing the ore; second, distributing the ore thinly over a wide, long, and open sluiceway; third, flowing the ore and propelling it forward over its bed by the action of a stream of chemical solution adapted to dissolve the ore; fourth, automatically screening and separating the solution from the tailings by the same force; and fifth, subjecting the solution to a reagent to precipitate the gold therein.

**727659—May 12, 1903.** F. W. MARTINO. *Method of extracting noble metals.*—The process of recovering gold from its cyanide solution, consisting in acidifying the solution and treating it at a raised temperature with barium sulphocarbide. The latter is manufactured by fusing two parts, by weight, of barium sulphate (baryta or heavy spar)  $\text{BaSO}_4$  in an electric furnace with one part of carbon.

**728397—May 19, 1903.** T. B. JOSEPH. *Gold-extracting process.*—The process of extracting gold and silver from ore containing the same when in a suitable condition, which consists in subjecting the said ore to the leaching action of a solution of water, cyanide of potassium, hydrate of calcium, peroxide of barium and carbonic-acid gas, the ore being agitated by compressed air.

**730835—June 9, 1903.** D. MOSHER. *Ammonia cyanide process of treating copper, nickel, or zinc ores containing precious metals.*—The process of treating refractory sulphur, tellurium, and arsenical ores containing copper, zinc, nickel, gold, and silver, consisting in first roasting such ores at a low red heat to transform the metals so transformable into sulphates, arsenates, or tellurates; then oxidizing reducing compounds by very dilute ammonia; and subsequently extracting the metals with an ammoniacal-cyanide solution containing an excess of cupric oxide or hydroxide over and above that necessary to form metallic cyanide double salts.

**731169—June 16, 1903.** O. A. ELLIS. *Apparatus for extracting metals from ores.*—An apparatus for extracting metals from ores, having in combination a receiving hopper having an inclined bottom, a discharge opening in said hopper, an inclined chute leading from said hopper and provided with a screen, a precipitating box connected with said inclined chute, means for causing a flow of chemical solution through said hopper, chute, and precipitating box, and means for passing a current of electricity through said precipitating box.

**731631—June 23, 1903.** J. T. TERRY, Jr. *Extracting gold or silver from slimes.*—An improvement in separating precious metals from slimes with which they are mixed, consisting in forming a solution with water, spraying said solution into tanks containing a cyanide solution made dense by the addition of salt, allowing the slime to settle through and into the solution, then drawing the clear liquor from the top through vertically disposed filters and discharging the sludge from the bottom into succeeding tanks containing a similar cyanide solution, allowing it to settle and again drawing off the clear liquor.

**731839—June 23, 1903.** G. A. BAHN. *Sulphuric acid process of extracting precious metals from solutions.*—The process of precipitating precious metals from solutions thereof, which consists in producing cyanide solutions of said precious metals, then acidulating with sulphuric acid said cyanide solutions, then immersing zinc in sheet, plate, or other form in the acidulated-cyanide solution containing the precious metals; the chemical action thereupon taking place in the solution, dissolving zinc and precipitating the precious metals; then recovering from the precipitate of the preceding operation the precious metals by filtering and melting, or other process.

**732605—June 30, 1903.** G. E. THEDE. *Process of leaching ores.*—The process of leaching ores which consists in mixing with the ore to be treated a cyanide solution, peroxide of hydrogen, and an oxide which is reducible by said peroxide of hydrogen.

**732639—June 30, 1903.** T. B. JOSEPH. *Gold-extracting process.*—The process of extracting gold and silver from ore containing the same, when in a suitable condition, which consists in subjecting said ore to the leaching action of a solution containing water, cyanide of potassium, bromine, hydrate of calcium, peroxide of barium, and carbon dioxide, said carbon dioxide being forced into the leaching solution simultaneously with compressed air.

**738758—September 15, 1903.** J. B. DE ALZUGARAY. *Extraction of precious metals from their ores.*—The process for extracting precious metals from their ores, consisting in first moistening the crushed ore with an alkaline solution and afterwards agitating it in a solvent solution and blowing through it an oxidizing agent composed of gaseous bromine, and its acid and oxyacid compounds dissolved in air, and finally recovering the metals from the solvent in any well-known manner.

**745490—December 1, 1903.**—T. J. GRIER. *Process of extracting precious metals.*—The process of extracting precious metals from slimes, consisting in directing the slimes into a settling-tank, drawing off the thicker portions of the slimes and depositing the same into a leaching-vat, of introducing a cyanide solution under pressure through perforations in the false bottom of the vat, causing the watery portions of the slimes to be displaced by said cyanide solution, then treating the charge with an air under pressure, and afterwards introducing through the false bottom of a vat a salt solution of greater density than the cyanide solution to displace the latter.

**745828—December 1, 1903.** E. B. HACK. *Process of extracting metals from ores.*—A cyanide process, consisting of the following steps in the order named: Caking the pulp by pressure under conditions allowing the moisture to escape; introducing a weak solution of the solvent simultaneously with the introduction of air under pressure; drying the pulp by passing air under pressure therethrough; introducing a stronger solution of the solvent simultaneously with the introduction of air under pressure; and finally drying the cake by air pressure.

**755951—March 29, 1904.** J. SMITH. *Process of treating ores.*—In the cyanide treatment of ores, the method of rendering insoluble in the cyanide solution ferrous oxide contained in a mass of moist crushed ore, which method consists in applying heat to said mass in the presence of air, previous to its treatment by the cyanide solution.

## CLASS 204—ELECTROLYSIS.

*Subclass 15—Aqueous Bath, Ores.*

61866—February 5, 1867. J. H. RAE. *Improved mode of treating auriferous and argentiferous ores.*—This invention consists in treating auriferous and argentiferous ores with a current of electricity or galvanism for the purpose of separating the precious metals from the gangue. In connection with the electric current suitable liquids or chemical preparations, such, for instance, as cyanide of potassium, are used, in such a manner that by the combined action of the electricity and of the chemicals, the metal contained in the ore is first reduced to a state of solution and afterwards collected and deposited in a pure state. Among the claims is one for the use of the platinum agitator as an electrode.

62776—March 12, 1867. J. H. RAE. *Improved mode of collecting gold and silver from sweepings, washings, etc.*—This invention consists in treating sweepings, filings, and washings containing gold or silver with a current of electricity or galvanism for the purpose of separating the precious metals from the impurities of foreign matter mixed with them. In connection with the electric current suitable liquids or chemical preparations, such, for instance, as cyanide of potassium, are used in such a manner that by the combined action of the electricity and chemicals the precious metals contained in the sweepings, filings, and washings are first reduced to a state of solution, and afterwards collected and deposited either as oxides or in a metallic state, and the operation of extracting or separating said precious metals from the sweepings, filings, or washings is attended with very little trouble and expense. During this operation the bath which contains the washings, filings, or sweepings acts as an electrode, and also as an agitator; and the third claim of the patent covers the use of this carbon electrode as an agitator.

90565—May 25, 1869. W. J. LYND. *Improved process of separating iron and other metals from potters' clay.*—The process of removing iron, copper, and other discoloring matters from potters' clay and other argillaceous substances by subjecting the clay, when in solution, to the action of one or more magnets, or by passing through the bath containing such solution a current of electricity.

239300—March 22, 1881. A. RYDER. *Apparatus for treating ores.*—The invention has reference to apparatus for reducing ores in which the ore, while in a heated state, is dumped suddenly into a liquid or chemical solution for the purpose of disintegrating the ore and separating the particles preparatory to amalgamation. And the inventor claims, in an apparatus for disintegrating ores preparatory to amalgamation, the insulated vessel or non-conductor of electricity, provided with a metallic or plated hopper, in combination with an electrical generator or battery and conducting wire or wires.

246201—August 23, 1881. E. REYNIER. *Electrochemical treatment of ores.*—The method of treating ores of zinc and lead for the production of electricity and recovery of the metals by acting upon said ores in a voltaic couple with an electrolytic liquid having caustic alkali as the base, and precipitating the metallic oxides from said liquid.

272391—February 13, 1883. A. THIOLLIER. *Process of and apparatus for extracting metals from their ores.*—In combination with an electrogenerator, a receptacle for conductively prepared ore or other material containing metal to be recovered, having attachments for the negative and positive polar conductors of the electrogenerator, arranged, as described, in electrical communication with the mass of conductive ore by means of the electrolytic solution, whereby reduction is effected when the current is passed.

286208—October 9, 1883. L. LÉTRANGE. *Process of and apparatus for reducing zinc ores.*—The process of reducing zinc ores and producing pure metallic zinc and sulphuric acid simultaneously therefrom, which consists in simultaneously roasting sulphuret ores and carbonate ores in the same or communicating chambers, and thereby converting both ores into soluble sulphates, then leaching these roasted ores, and then depositing the metallic zinc from a solution of the sulphates by



electric currents on metallic plates, and drawing sulphuric acid at the same time from the solution as fast as set free by the said electric currents; and the apparatus for use in the process of reducing zinc ores, which consists, essentially, in a reservoir for the sulphate solution; a precipitating vessel provided with suitable anodes and cathodes; a pipe provided with a regulating cock, leading from the reservoir to near the bottom of the precipitating vessel, and an outlet pipe for the freed acid, arranged in the said vessel at the desired level of the liquid therein, whereby the strength and quantity of the sulphate solution in the precipitating vessel are maintained constant.

291670—January 8, 1884. M. BODY. *Process of and apparatus for obtaining gold and silver from their ores by combined electrolytic and amalgamating processes.*—The method of first subjecting gold and silver ores to the action of ferric salts, in combination with the electrolytic process, and the subsequent amalgamation of the metals with mercury under the continued action of the electric current; and the apparatus for effecting this process.

300950—June 24, 1884. H. R. CASSEL. *Process of and apparatus for the separation of metals from ores and alloys.*—The process of separating metals from ores or alloys, especially those of an auriferous character, which consists in charging the ore or alloy in a powdered condition into an anode compartment, which is separated from the cathode compartment by porous material, said anode compartment containing a solution yielding nascent chlorine under the action of an electric current, and agitating said powdered material within said solution during the passage of the electric current; and the combination in an apparatus for treating ores and metals by electrolysis, of a cathode compartment, a negative pole therein, a rotary drum constituting the anode compartment, provided with porous material separating it from the cathode compartment, and with a series of carbon rods or plates arranged within the same, and suitable electric connections.

300951—June 24, 1884. H. R. CASSEL. *Process of chloridizing ores by electrolysis.*—In the process of extracting gold from rebellious or refractory gold ores, the steps which consist in subjecting the ore to the action of a solution yielding nascent chlorine under electrolytic decomposition, and adding lime or its equivalent, whereby acids formed by secondary action during said decomposition are neutralized.

317245—May 5, 1885. E. P. THOMPSON. *Apparatus for the separation of gold from its ores by electrochlorination and deposition.*—The combination, with an electrolytic cell for separating chlorine from its compounds and its anode, of a battery, a cathode consisting of a pipe through which steam is admitted to the cell for the purpose of increasing the rapidity of the separating, and conductors respectively connecting the same anode and cathode with the poles of said battery.

317246—May 5, 1885. E. P. THOMPSON. *Apparatus for the electrodeposition of gold from its chlorides.*—The combination, in an electrolytic cell, of an anode formed of a series of carbon rods set in a metal ring, and a cathode formed by two thin corrugated copper plates connected electrically, which are set, respectively, within and without the circle of carbons.

332705—December 22, 1885. H. H. EAMES. *Apparatus for chloridizing gold, silver, and other ores.*—This invention consists of an iron vessel cylindrical in shape, lined with wood, having a cast-iron cover, adjusted so as to be steam- and vapor-tight. It is also arranged with a set of stirrers, to which motion is communicated by crown- and pinion-wheels. It is also fitted with pipes, by means of which steam can be forced through the contents and held there under pressure. It is also furnished with two electrodes, by which electricity can be passed through the ore and chemicals operated upon, while the pressure is applied. The electric current is best obtained from a dynamo machine of ordinary construction used in the deposition of metals.

333815—January 5, 1886. M. BODY. *Process of obtaining gold, silver, copper, nickel, and cobalt from their ores by electrolytic action.*—The process of separating gold, silver, copper, and other metals from chlorinated or chlorine-containing ores by electrolytic action, consisting in first roasting the ores or subjecting them

to an equivalent oxidizing treatment, as specified, and then subjecting the ore to the action of ferric-salt solutions, and at the same time passing an electric current through said solution, whereby the metal becomes dissolved and precipitated, and chlorine gas is generated at the positive pole, which reconverts the resulting ferrous salts into ferric salts.

**351576—October 26, 1886.** H. R. CASSEL. *Process of extracting gold, etc., from ores.*—The process of separating metals from ores or alloys, especially those of an auriferous character, which consists in charging the ore or alloy in a powdered condition, into an anode compartment, which is separated from the cathode compartment by a porous partition composed of asbestos, which permits the passage of the current with the metals in solution, and retains the ores within the anode compartment, said anode compartment containing a chloride solution, agitating and subjecting the charge to nascent chlorine produced from said solution during the passage of the electric current, passing the solution of metals through the asbestos partition, and depositing the metals in solution at the cathode.

**357659—February 15, 1887.** D. G. FITZGERALD. *Obtaining chlorine by electrolysis.*—The electrochemical generation of chlorine by means of an anode of peroxide of lead in the form of dense, highly conductive layers, plates, or masses of any required form preferably obtained by the means hereinbefore described, the said anode being employed in conjunction with any suitable cathode and with an electrolyte capable of evolving chlorine.

**360852—April 12, 1887.** H. R. CASSEL. *Apparatus for separating metals from ores or alloys.*—In an apparatus for separating metals from ores or alloys by electrolysis the combination of a journaled drum provided with carbon anodes, a hollow metallic shaft insulated on its exterior and extending through said drum, said shaft being perforated within the drum and separated from the interior thereof by a filter, and a screw conveyor within said hollow shaft.

**360853—April 12, 1887.** H. R. CASSEL. *Apparatus for separating metals from ores or alloys.*—In an apparatus for separating metals from ores or alloys by electrolysis the combination of a rotary drum constituting the anode compartment and having a suitable electric connection, a rotary cathode compartment having a suitable electric connection and provided with an automatic valve, a porous diaphragm separating said anode and cathode compartments, a fixed bracket, and an arch-shaped arm attached to said bracket in the path of said valve for opening of the latter.

**362022—April 26, 1887.** H. LIEPMANN. *Apparatus for separating metals from ores or alloys by electrolysis.*—In an apparatus for separating metals from ores or alloys by electrolysis the combination of an anode compartment, a cathode compartment, a filtering diaphragm separating said compartments, a dense porous diaphragm for separating said compartments during one step of the operation, and mechanism whereby the dense porous diaphragm may be placed in opposition with or removed from the opening between the anode and cathode compartments.

**379764—March 20, 1888.** C. F. CROSELMIRE. *Wet process of extracting pure zinc from its ores.*—The process which consists in immersing roasted zinc ore in dilute acid, passing an air blast through the solution until the impurities are oxidized, and finally drawing off the zinc solution and depositing or precipitating the zinc.

**387036—July 31, 1888.** C. P. BELLOW. *Process of cleansing gold and silver where mechanically coated in ores with refractory substances.*—The process of cleansing refractory ores prior to the recovery of the precious metals therefrom, which consists in immersing said ores in a solution of a sodium chloride and caustic soda, heating said solution, and at the same time subjecting the ores to the action of the electric current, whereby the ore is rendered free milling.

**391360—October 16, 1888.** H. H. EAMES. *Apparatus for chloridizing ores.*—In a device for chloridizing metallic ores, the combination of a hermetically sealed tank, metallic plates placed inside the said tank and mounted upon insulated supports, whereby they will be insulated from each other and from the tank, the said plates forming the two elements of a galvanic battery, a stirrer placed in the said

tank and between the said plates a solution containing the ore to be treated, by which a galvanic current will be excited between the said charging steam in the said tank, whereby the said solution will be heated and a pressure maintained in said tank.

399209—March 5, 1889. J. H. RAE. *Electric amalgamator*.—In an apparatus for working ores, a pan or tub with an internal copper ring and rotating arms or stirrers, in combination with a horizontal wooden ring suspended above the tub, a copper plate forming the upper surface of said ring and perforated to admit carbons which pass loosely through the plates, said carbons having heads or transverse pins at the upper ends, and the movable elastic plates or springs pressing upon the heads of the carbons to hold them in contact with the copper plate.

407386—July 23, 1889. J. C. WISWELL. *Bath or solution for separating metals from their ores*.—The process of producing a bath or solution for the separation of metals from their ores, consisting in subjecting a solution of salt water, muriate of ammonia, and muriatic acid to a current of electricity, then placing this solution in a tank containing liquid mercury, and subjecting the whole to a current of electricity, said mercury serving as the anode.

410228—September 3, 1889. J. C. WISWELL. *Solution for use in separating metals from their ores*.—A solution or bath for use in separating metals from their ores, consisting of chlorine in solution, sodium chloride, ammonium chloride, hydrochloric acid, and bichloride of mercury.

415576—November 19, 1889. W. VON SIEMENS. *Process of electrodeposition of metals*.—The process which consists in lixiviating ore in separate vessels with a solution containing ferric sulphate, passing the resulting ferrous sulphate successively through a series of compartments containing cathode plates, and in which cells the solution is subjected to the action of an electrical current by which the metal in solution is deposited, then passing the remaining liquid successively through a second series of compartments containing anode plates of insoluble material and separated from the first-mentioned compartments by non-metallic diaphragms, whereby the ferrous sulphate is oxidized and reconverted into ferric sulphate, which solution is again used to lixivate ores.

418134—December 24, 1889. H. F. JULIAN. *Process of extracting gold and silver from their ores*.—The improvement in the process of extracting gold and silver from ores, which consists in agitating the pulverized ore in closed vats with chlorine, bromine, or iodine and water under pressure of a fluid forced into the vat, and after the gold and silver have combined with the halogen, adding mercury and again agitating under pressure of a fluid forced into the vat, next passing the ore, mercury, and solution over amalgamated copper surfaces forming the cathode of an electric circuit, and subsequently submitting the mixture to electrolytic action between cathodes of mercury below and suitable anodes above.

452125—May 12, 1891. W. VON SIEMENS. *Apparatus for extracting metals from their ores*.—The combination of a trough for the flow of liquid, composed of numerous sections connected at alternate ends, with an inlet at one end and an outlet at the other, with two longitudinal shafts in each section of the said trough, said shaft carrying beaters and being entirely immersed in the liquid contained in the trough, and a heating pipe located below and between the said shafts.

459023—September 8, 1891. C. SCHREIBER and H. KNUTSEN. *Process of extracting antimony from ores*.—In the extraction of antimony from ore, the process which consists in subjecting the crushed ore to the action of a solution of sulphide of sodium and then precipitating the antimony in metallic form by electrolysis, adding hydroxide of sodium to the solution.

460354—September 29, 1891. W. VON SIEMENS. *Apparatus for electrolytically separating metals from ores*.—In an electrolytical cell, the combination of a revolving cathode, a trough-shaped anode situated below the said cathode, in the trough of which the cathode revolves, a screen permitting the passage of the electrolyte and of electricity and capable of preventing the passage of vibrations of the electrolyte situated between the said cathode and anode, and means for supplying the electrolyte above the screen and for withdrawing the oxidized liquid from the bottom of the trough of the anode.

473105—April 19, 1892. G. J. ATKINS. *Electrolytic apparatus for separating gold and other metals from their ores.*—Electrolytic apparatus for separating gold and other metals from their ores, which consists of an upright anode compartment through which the ore is passed continuously, having within it an anode constructed to receive and retard the descent of the ore, while the ore itself forms a more or less soluble portion of such anode pole, and an upright cathode compartment and pole, the said anode and cathode compartments communicating through an opening closed by a porous diaphragm and having outlets at their lower ends for the removal of the ore which has been acted upon in the anode compartment and of the metals and other substances that have been deposited or precipitated in the cathode compartment.

484869—October 25, 1892. G. J. ATKINS. *Process of separating gold and other metals from their ores.*—The continuous process of separating gold and other metals from their ores, which consists in passing such ore through the anode compartment of an electrolytic apparatus in contact with the anode and retarding the descent of the ore in the said anode compartment while such ore is kept in contact with the anode pole of such compartment, so as to form a more or less soluble portion of such anode pole, and then subjecting the ore to the process of amalgamation.

495212—April 11, 1893. J. F. WISWELL. *Process of and apparatus for treating ores.*—An improved process of treating ores which consists in submerging mercury in a solution of common salt connecting the mercury with the positive pole of a generator and the salt solution with the other pole, so that the current will decompose the salt solution and cause the chlorine to be attracted to the mercury forming calomel; treating the calomel with aqua regia forming a soluble mercuric chloride, diluting the latter with water, treating undecomposed salt solution with an electric current to produce sodium hypochlorite and introducing the soluble mercuric chloride and sodium hypochlorite simultaneously upon the crushed ore.

495637—April 18, 1893. J. PFLEGER. *Process of extracting zinc by electrolysis.*—The process of obtaining zinc by electrolysis out of a zinc-containing anode, which consists in adding to the bath a basic zinc-salt solution adapted to act as electrolyte, to which basic zinc-salt solution a conducting neutral salt has been added.

495715—April 18, 1893. S. R. WHITALL. *Process of lixiviating ores.*—The process of separating gold and silver from their ores, which consists, first, in roasting the ore to oxidize the base metals; and, secondly, in subjecting the roasted ore to the action of a solution of potassium cyanide and sodium hyposulphite, and subsequently precipitating the dissolved metals; and the process of separating gold and silver from siliceous ores, which consists in subjecting the ore admixed with caustic soda and potash to the action of a solution of potassium cyanide and sodium hyposulphite.

497014—May 9, 1893. F. W. CLEGHORN. *Process of separating precious metals from ores.*—The process of separating gold and silver from ores, consisting in filtering through the ores a solution of sulphuric acid and salt, and precipitating the gold and silver in the filtrate solution by placing metallic iron in the filtrate and passing an electric current through the filtrate.

501997—July 25, 1893. S. H. EMMENS. *Apparatus for the electrolytic extraction of metals.*—In apparatus for the electrolytic extraction of metals, a vat having an anode lining on its floor and sides, in combination with a suitable cathode or cathodes suspended within the vat and a non-porous and non-conducting inner wall or curb located between the side linings and the cathode or cathodes and extending from the upper surface of the floor lining to above the surface of the electrolyte, and serving to support a lining of the substance to be acted upon in contact with the anode side linings and to prevent short-circuiting between said anode side linings and the cathodes.

507130—October 24, 1893. C. HOEFFNER. *Electrolytic production of metals.*—The process of obtaining copper and silver free from other metals, which consists in forming a cuprous-chloride solution of these metals by leaching a cupriferous

and argentiferous material with a cupric-chloride solution containing a solvent for cuprous chloride, separating from the cuprous-chloride solution so obtained such metals as arsenic, antimony, cobalt, and the like, extracting the silver by precipitation, electrolyzing the cuprous-chloride solution, preventing the solution at the anode from commingling with the solution at the cathode, mixing together the two solutions after having been acted upon by the electric current and preventing an accumulation of iron therein by oxidizing and removing the latter.

512361—January 9, 1894. P. C. CHOATE. *Art of producing metallic zinc.*—The method of producing from an impure solution of zinc salts a zinc electrolyte free from depositable impurities, which consists in subjecting the solution to the action of an electric current to precipitate and deposit the depositable impurities, and at the same time preventing the resolution of such impurities in the solution by neutralizing the acid set free in the bath with a neutralizing agent which is free from any depositable impurities soluble in the solvent element of the bath.

512362—January 9, 1894. P. C. CHOATE. *Process of preparing solutions carrying salts of zinc.*—The process of forming a solution carrying salts of zinc, which consists in forming a sulphate solution of the soluble elements of the ore and recovering the same therefrom by evaporation and crystallization, heating the crystallized product to drive off the salts of metals more volatile than zinc and convert those less volatile than zinc into compounds insoluble in water and finally treating the mass with water to dissolve the zinc element.

518732—April 24, 1894. P. C. CHOATE. *Art of producing metallic zinc.*—The process of continuously producing metallic zinc by electrolysis, which consists in depositing the zinc from an acidulated solution of a zinc salt, drawing off from the bath the free acid liberated therein, dissolving in such acid oxidized zinc, in the state of fume, freed from its more volatile soluble impurities, and returning the solution thus formed to the bath from time to time, as required, to maintain the electrolyte.

526099—September 18, 1894. P. DANCKWARDT. *Apparatus for and process of extracting gold or silver from ores.*—The process of extracting gold and silver from ores, which consists in subjecting the same simultaneously to the action of cyanide of potassium, an alkali sulphide, and to electrolysis; and the combination of a main apparatus consisting of a revolving outer drum having blades, an insulated inner drum and electric connections, with an auxiliary apparatus consisting of a series of communicating tanks, rotating insulated drums and electric connections.

528023—October 23, 1894. L. PELATAN and F. CLERICI. *Extracting gold from its ore.*—The combination with a crushing mechanism and an amalgamator, of a series of vessels containing a solution of cyanide of potassium and a salt of sodium, each vessel having an amalgamated copper bottom connected to one pole of a generator of electricity and a central shaft having a zinc pipe and agitator connected to the other pole, a filter, a series of communicating closed vessels of lead, each containing a body of aluminum chips resting on a perforated diaphragm above the inlet and rising nearly to the outlet, and means for creating a vacuum beneath the filter to drive the fluid through and into the series of lead vessels under pressure.

531169—December 18, 1894. V. ENGELHARDT. *Process of extracting metals from sulphide ores, etc.*—The process of treating the sulphur compounds of metals, which compounds have combined therewith other ore compounds not soluble in a solution of an alkaline sulphhydrate, which consists in extracting the sulphur compounds by treatment with an alkaline sulphhydrate, thereby also generating sulphureted hydrogen, subjecting the solution thus formed to the action of an electric current in the cathode compartment of an electrolytic cell, in the anode compartment of which is an alkaline chloride, thereby obtaining the metals, reforming the sulphhydrate, and liberating free chlorine, treating the ore residues, resulting from the sulphhydrate bath with such chlorine, and subjecting the solution thus obtained to the action of the sulphureted hydrogen first generated in the sulphhydrate bath.

537423—April 9, 1895. F. H. LONG and D. C. SKADEN. *Apparatus for recovering precious metals from their ores.*—An apparatus for recovering precious metals

comprising a revoluble drum, a perforated metal tube opening from said drum and provided with a fabric jacket, a series of plates secured to the inner surface of the drum and having inwardly extended blades or flanges, electric connections to the plates and tube for rendering the same of opposite polarity, a rotatable conveyor located and working in said tube and a fixed vent-pipe passing axially through the drumhead and opening into the interior of the drum near the top thereof.

538522—April 30, 1895. E. D. KENDALL. *Process of and reagent for recovering silver and gold from solutions.*—The process of the recovery of gold and silver from solutions, which consists of the following steps: First, the subjecting of the ore containing the precious metals to the action of a solvent, thus obtaining an aqueous solution of the solvent and the minerals contained in the ore; second, subjecting the said solution to the electrochemical action of a mercurial amalgam; third, subjecting the valuable precipitate secured by the preceding process to the action of dilute acid in the presence of carbon; fourth, the recovery of the valuable metal from the result of the preceding process.

545546—July 30, 1895. E. J. FRASER. *Process of and apparatus for treatment of precious metals.*—The process of separating gold or other precious metal held in an electrolytic solution, which consists in passing the solution through a vessel containing alternating porous layers of zinc and carbon, to set up a local voltaic action which tends to decompose the solution, precipitating the gold in the carbon by filtration.

543673—July 30, 1895. M. CRAWFORD. *Process of extracting precious metals from their ores.*—The improved process of removing precious metals from their ores which consists, first, in lixiviating the ore with a cyanide solution which has been subjected to the action of an anode separated from its corresponding cathode by a porous partition which substantially prevents the circulation of the electrolyte; second, in withdrawing said solution and removing the precious metals therefrom; third, in again subjecting the solution to the action of an anode separated from its corresponding cathode as before and using it over again in continuous rotation.

543674—July 30, 1895. M. CRAWFORD. *Process of extracting precious metals from their ores.*—The improved process of extracting precious metals from their ores, which consists in forming a solution of a cyanide and a cyanate of the corresponding base, the total amount of cyanate being not less than 25 per cent. of the total amount of cyanide present; lixiviating the ore therewith and extracting the dissolved precious metals from said solution.

543675—July 30, 1895. M. CRAWFORD. *Apparatus for extracting precious metals from their ores.*—An apparatus for extracting precious metals from their ores, which consists in the combination of a tank wherein the solvent liquid is stored; a revoluble lixiviating receptacle; a pipe running from said storage-tank to the lixiviating receptacle; an amalgamating table; means for causing the lixiviating receptacle to discharge its contents continuously upon the amalgamating table; a separating-tank; means for conducting ore which has passed over the amalgamating table into the separating-tank; means for separating the solid contents of this separating-tank from its liquid contents; a third tank; connections whereby the solvent liquid thus separated is passed to said third tank; means for reclaiming the precious metals from the solution in said third tank; and connections whereby the solvent liquid is run from the third tank to the storage-tank; and a separator for removing the tailings of the ores of precious metals from their accompanying solvent solution, which consists in the combination of a tank into which the ores and solution are discharged; a conveyor running from the bottom of said tank to a point exterior thereto by which the solids are separated from the liquids; a car-filter with a permeable bottom situated below the discharge end of the conveyor; and a second tank below said car-filter.

544610—August 13, 1895. E. W. CLRAK. *Process of and apparatus for extracting ores by electrolysis.*—In an electric chlorinator for gold ores, the combination of the hollow cylinder constructed in longitudinal sections united by bands, and having the series of separate boxes or chambers communicating with its interior;

the electrical connections consisting of the anode in the cylinder chamber, and the cathodes in the boxes or amalgamating chambers, the agitator-shaft provided with the spirally-arranged series of stirrer-arms and adapted to revolve in the cylinder chamber, and the stuffing boxes at the ends of the cylinder.

546873—September 24, 1895. E. A. ASHCROFT. *Process of treating zinc-bearing ores.*—In the treatment of zinc-bearing ores and zinc-bearing products, the method of simultaneously depositing zinc from a catholyte free from iron, and raising a ferrous-salt solution to the ferric state, which consists in passing the zinc-bearing solution free from iron, around the metallic cathodes of an electrolytic apparatus, and simultaneously passing the ferrous-salt solution around the insoluble anodes of the said electrolytic apparatus.

549907—November 19, 1895. A. L. ELTONHEAD. *Apparatus for extracting gold.*—In an apparatus for extracting gold and other metals, the combination of a mercury receiving-box, a horizontally movable vessel therein, having its lower end open and unobstructed whereby mercury placed within the box may, in seeking its level, enter said vessel, a horizontally placed anode strip suspended within the latter, means for adjusting the strip vertically, a cathode connection and conductor wires adapted to connect the anode and cathode with a suitable dynamo or battery.

551648—December 17, 1895. L. PELATAN and F. CLERICI. *Electrolytic process of obtaining precious metals.*—In an apparatus for the extraction of precious metals by direct electrolytic action, the combination with an electrolytic vat having cathodes arranged at its bottom, of anode cylinders arranged above the said cathodes, anode plates alternating with said cylinders, a generator of electricity having its poles connected to said anode cylinders and plates and to the cathodes, means for rotating the anode cylinders which are provided with agitators, a force-pump having injection-pipes to discharge beneath the anode plates and cylinders, said pipes being provided at or near their mouths with interior, concentric rods having spiral ribs, or feathers, and suction-pipes having their open ends arranged above the anode plates.

552960—January 14, 1896. C. HOEPFNER. *Process of producing cuprous oxides.*—The process which consists in leaching cupriferous materials with a cupric chloride solution containing calcium chloride, whereby a solution containing cuprous chloride is obtained, converting the cuprous chloride in a portion of the solution into cupric chloride by means of a suitable acid as sulphurous acid in the presence of oxygen, freeing the other portion of the solution from metals other than copper, and converting the cuprous chloride therein into cuprous oxide by means of a suitable reagent, as caustic lime.

553816—January 28, 1896. L. PELATAN and F. CLERICI. *Process of and apparatus for extracting gold from its ores.*—A single continuous process for the extraction of precious metals from their ores, and the amalgamation of the same which consists in treating said ores with a comparatively weak solution of a soluble cyanide, such as cyanide of potassium, adding thereto a peroxide, such as hydrogen binoxide, increasing the electric conductivity of said solution by adding chloride of sodium, increasing the solvent power of said solution by passing a relatively weak current of electricity through the same, retaining the sodium chloride in the solution practically without decomposition and continuously revolving the anode in the solution over a fixed cathode of mercury.

556092—March 10, 1896. O. FRÖLICH. *Process of extracting noble metals from ores.*—The process of extracting precious metals from a lye containing also inferior metals, said lye containing substantially five grains of each of the said metals to the pint, which consists in subjecting the said lye to the action of an electric current of substantially twelve amperes for each two square yards of cathode surface, whereby the gold is separated by electrolysis.

563143—June 30, 1896. J. DOUGLAS. *Process of extracting copper from ores.*—The method of extracting copper from solid cuprous chloride, which consists in moistening said solid cuprous chloride with water, inserting both electrodes of an electric circuit in the said solid cuprous chloride, and then passing an electric current therethrough.

563144—June 30, 1896. J. DOUGLAS. *Process of extracting copper from ores.*—The process of extracting copper from the solid cuprous chloride, which consists in suspending the said solid cuprous chloride in an acidulated electrolyte, inserting the cathode of an electric circuit into the solid cuprous chloride, and the anode into the electrolyte, and passing an electric current therethrough.

566894—September 1, 1896. P. DANCKWARDT. *Apparatus for extracting gold and silver from ore.*—The combination of a revolving barrel having an amalgamated copper lining with non-conducting bottoms, a series of inclined perforated metal strips secured to such bottoms, insulating rings that sustain the bodies of such strips, and with electric connections that communicate with the barrel and the strips.

566986—September 1, 1896. R. KECK. *Cyanide process of extracting precious metals from their ores.*—The process of extracting precious metals from their ores, which consists in dissolving said metals in a cyanide solution and extracting them therefrom by electrolytic precipitation effected by alternating plates of lead and aluminum, the former being anodes and the latter cathodes.

567503—September 8, 1896. L. PELATAN and F. CLERICI. *Process of extracting gold and silver from their ores.*—The process, which consists in submitting the ores of gold and silver to the action of a comparatively weak cyanide solution containing chloride of sodium, intensifying the solvent power of the solution by the passage of a continuous electric current having an electromotive force below that required for the decomposition of sodium chloride and continuously revolving the anode from which the current is supplied to the solution over a mercury cathode.

568099—September 22, 1896. L. PELATAN and F. CLERICI. *Electrolytic apparatus for extracting gold and silver from their ores.*—The combination with a vat having a flat bottom, of a cathode of mercury spread thereon, an anode having the form of an endless belt, rolls arranged near the ends of the vat to support and give continuous movement to said anode in parallelism with the surface of the cathode, and means for imparting continuous movement to said anode, in one direction, it being provided with stirring devices moving with it.

568724—October 6, 1896. E. ANDREOLI. *Apparatus for electrodeposition of gold or silver.*—In an apparatus for the electrodeposition of gold and silver from a solution, a tank provided with one or more anodes and a series of amalgamated cathodes, each cathode consisting of perforated, skeleton, or network plates and a layer of mercury in the bottom of the tank into which each of the cathodes dips, said layer of mercury being connected with the negative pole of electricity, thereby constituting a common vehicle for the current from all the cathodes while at the same time maintaining the said cathodes constantly amalgamated.

568741—October 6, 1896. H. R. CASSEL. *Process of extracting gold from substances containing it.*—The process of extracting gold from ores, which consists in decomposing a bromide of an alkaline base by electrolysis, dissolving the gold by the anode solution, adding the cathode solution, running the product through a mixture of iron and carbon to precipitate the gold, and redecomposing the liberated bromine solution by electrolysis.

568843—October 6, 1896. V. ENGELHARDT and A. NETTEL. *Process of treating metallic sulphides.*—The process of treating a metallic sulphur compound, which consists in first converting the said compound into a soluble double sulphide by treating it with any suitable reagent, such as the sulphhydrate of calcium in aqueous solution; then decomposing the resulting solution by electrolysis to produce the metal and sulphureted-hydrogen gas, then treating the spent solution with carbonic-acid gas to precipitate a carbonate of the base and liberates sulphureted-hydrogen gas, then recovering the oxide of the reagent and the carbonic-acid gas from the precipitate by calcination, then combining the sulphureted-hydrogen gas given off during the process with the said oxide to form more reagent, and using the recovered carbonic-acid gas to treat more spent solution.

571468—November 17, 1896. T. P. BARBOUR. *Process of treating ores.*—The process of treating ores, which consists in first treating the raw material with copper oxide and sulphuric acid, then chlorinating the pulp thus treated, introducing the chlorinated mass into a suitable agitator having zinc therein, and establishing an electric current through the mass in the presence of zinc; and a chlor-



inating-tank for treating ores consisting of a revoluble cask having a single man-hole and a circular series of bugholes, copper pole disks secured within the cask at opposite ends thereof and arranged in an electric circuit, insulator bracing posts arranged between said disks and the outer heads of the tank, flanged guide-rings encircling said cask at an intermediate point, spur-rings encircling the cask near its opposite ends, and a horizontal drive-shaft carrying guide-rolls engaging said flanged guide-rings and drive-pinions engaging said spur-rings.

573233—December 15, 1896. M. NETTO. *Process of precipitating precious metals from their alkali-cyanide solutions.*—The process of precipitating silver and gold from their alkali-cyanide solutions, which consists in acidulating the alkali-cyanide solution containing said metals with hydrochloric acid so as to precipitate silver chloride, separating said silver chloride by filtration, subjecting the acid filtrate to the action of the electric current so as to deposit the gold on the cathode, and regenerating the cyanide solution by the addition of caustic alkali.

578171—March 2, 1897. C. P. TURNER. *Electrolytical apparatus.*—An electrolytic apparatus, provided with an anode consisting of a non-conducting receptacle coated with an anti-corrosive substance and provided with an outer coating of a conducting material and means for connecting said outer coating with the positive pole of a source of electrical supply.

579872—March 30, 1897. J. H. HAYCRAFT. *Process of treating auriferous and argentiferous ores.*—The process of treating ores consisting in introducing the ore into a pan, adding thereto mercury and soluble salts capable of yielding chlorine by electrolysis, raising the ore contents of the pan to about the boiling-point of water and passing a current of electricity through the heated mass while stirring the same to secure a simultaneous electrolytic chlorination and electro-amalgamation, and maintaining the anode out of vertical alignment with the mercury cathode.

581160—April 20, 1897. H. HIRSCHING. *Process of treating ores containing silver and gold.*—The process of treating ores, which consists in subjecting them in the presence of moisture to the action of ammonia and a nitrate, and then precipitating the metal or metals from the resulting solution.

582077—May 4, 1897. E. MORTZ. *Apparatus for extracting precious metals.*—In an apparatus for extracting precious metals, the combination of a rotative drum provided with a manhole and having a valved connection for the admission of compressed air, a core of insulating material mounted to turn in the said drum, metal plates forming the positive and negative electrodes of an electric circuit and arranged respectively on the drum and core, and an electrical connection for said plates on the core, the said connection being arranged to lock the drum and core together.

584242—June 8, 1897. P. G. SALOM. *Process of making commercial lead from lead ore.*—The process of converting lead ore into commercial lead, without the application of heat, by subjecting the ore to the action of nascent hydrogen, electrolytically developed, producing thereby a spongy mass, and afterward, while the mass is in a non-oxidized condition, applying a consolidating pressure.

585355—June 29, 1897. C. A. BURGHARDT and G. RIGG. *Process of obtaining metallic zinc and copper from ores.*—The improved process of recovering metallic zinc and metallic copper from cuprous zinc ore, which consists in treating the roasted and ground ores with an ammoniacal solution, then in freeing the resultant liquid from iron dissolved by said solution, then in depositing the metallic copper on suitable metallic plates acting as a couple, and in finally effecting the electrolytic deposition of the metallic zinc.

585492—June 29, 1897. J. F. WEBB. *Method of an apparatus for separating precious metals from their solvent solutions.*—The improved method of separating precious metals from a solvent solution containing the same, consisting in passing the solution alternately through a body of carbon and zinc, and subjecting the same in its passage to an air current; and a metallurgical filter for this purpose containing the same, consisting of a series of alternate compartments, or receptacles, containing, respectively, carbon and zinc, through which the solvent solu-

tion is passed with an upward and downward flow, and electric circuit completing connection between the zinc and carbon.

588076—August 10, 1897. B. MOHR. *Process of treating sulphide ore.*—The process for treating sulphide ore by acting on the pulverized ore with acid sodium or potassium sulphate, so as to obtain a solution of sulphate of zinc, depositing the zinc by electrolysis and thus recovering the acid alkali sulphate, and treating the insoluble residue obtained by the lixiviation for recovery of the other metals.

588740—August 24, 1897. B. BECKER. *Apparatus for treating gold and silver ores.*—In apparatus for the treatment of gold and silver ores the combination of a vat provided with amalgamating plates and adapted to contain cyanide of potassium, in solution, and the ore to be treated, a vat containing the electrodes of an electrolytic apparatus and means for causing the circulation of the cyanide of potassium solution through the amalgamating vat, and for distributing it in the electrolytic vat.

598081—September 28, 1897. W. L. BROWN. *Process of treating rebellious ores.*—The process of treating ores finely divided and mixed with water, which consists in adding a suitable compound to said ores and water, which compound contains an element which has a chemical affinity for the base constituents of the ore, then passing an electric current through said material to unite the said element chemically with the base constituents and to liberate the precious metals, then circulating the material over an amalgamated surface which is not in the electrical circuit, and finally returning the material again through the field of electrolytic action.

598055—October 19, 1897. E. C. KETCHUM. *Process of treating ores.*—The process of treating mixed sulphide ores containing lead and zinc, which consists in first roasting the ores, then subjecting the roasted ores to the action of a solution of caustic alkali in the presence of heat to remove from the ores the lead and the zinc, then subjecting the caustic solution containing the lead and zinc to electrolytic action in one or more cells to remove the lead, the anodes of which cells are immersed in a volume of pure caustic solution, which is separated by a porous medium from the electrolyte containing the lead and zinc, and then subjecting the caustic solution or electrolyte containing the zinc only to electrolytic action in one or more cells to remove the zinc.

592973—November 2, 1897. E. MORZ. *Electrolytic apparatus.*—In an electrolytic apparatus the combination with a frame or sluice of a series of convex cathode plates located in the bottom of said frame or sluice, a series of anode plates having curved under faces and disposed above said cathode plates, blocks secured to the anode plates and supported in the frame or sluice, each block having a recess in its upper edge, a series of conductors connected with said anode plates and terminating in said recesses in the blocks, a conducting rod disposed in said recesses on the first-mentioned conductors and having a notch therein, a cross-bar passing through said notch, a conductor with which said cross-bar is electrically connected, locking devices for securing the cross-bar to the frame or sluice, and a conductor connected with the cathode plates.

594611—November 30, 1897. S. H. EMMENS. *Process of and apparatus for removing zinc from zinciferous ores.*—The process of treating zinciferous ores, which consists in pulverizing and roasting the ore, leaching it in a series of vessels through which the solution flows continuously, and subjecting the contents of each vessel intermittently to electrolytic action, whereby the solution is rendered alternately acid and neutral or more acid and less acid in contact with each body of ore; and an apparatus for treating zinciferous ores, comprising a series of leaching-vats, each provided with an inlet-pipe extending to the bottom and with an exit-pipe or trough leading from the top of the vat, and each provided at bottom with an insoluble anode, a series of movable cathodes suspended above said vats, means for raising and lowering the cathodes of adjoining vats alternately, and an electric circuit to the respective poles with which said anodes and cathodes are connected.

597820—January 25, 1898. N. S. KERR. *Art of obtaining gold and silver from auriferous and argentiferous materials.*—The process of obtaining a precious metal from its ores, which consists first in dissolving the gold or silver in a cyanide solution containing cyanide of mercury and free cyanide of an alkaline metal, such

as cyanide of potassium, and then passing a current of electricity through said solution to a metallic cathode, whereby an easily removable layer of the precious metal and mercury is simultaneously deposited upon said cathode.

598193—February 1, 1898. E. ANDREOLI. *Apparatus for electrodeposition of gold and silver.*—In apparatus for the electrodeposition of gold, silver, or other metals, anodes of peroxidized lead acting in the presence of and in combination with a cyanide or cyanide-compound solution.

600351—March 8, 1898. E. A. ASHCROFT. *Treatment of metalliferous ores and products.*—The improved process of preparing a solution suitable for leaching zinc-bearing ores of zinc-bearing products, consisting in electrolyzing a zinc-bearing solution successively in contact with a suitable cathode and an anode resulting from the preliminary furnace treatment of products or ores containing copper and iron, and then depositing the copper from the resulting ferrous solution, and simultaneously raising the iron content of such solution to the ferric state by electrolyzing the said resulting ferrous solution successively in contact with suitable cathodes and insoluble anodes.

601068—March 22, 1898. F. W. WHITRIDGE. *Method of and apparatus for extracting gold from its ores.*—The method of extracting gold from a weak cyanide solution, which consists in circulating the solution over anodes of iron and cathodes of lead, said cathodes being formed of thin plates arranged at short distances apart and having from 9 to 10 square meters of surface for each ton of solution in contact with them; and subjecting the said solution while in motion to an electric current of from 3.5 to 4 volts, and of from 0.5 to 1.5 amperes per square meter of cathode surface; and in apparatus for obtaining gold from a weak cyanide solution by electrolysis, the combination with a cell provided with anodes of iron and cathodes of lead formed of thin plates, said cathode plates having from 9 to 10 square meters of surface to each ton of solution in the cell; of means for circulating the solution in the cell, and means for subjecting the solution to a weak current of electricity.

603904—May 10, 1898. J. R. HEBBAUS. *Apparatus for extracting precious metals.*—An apparatus for extracting precious metals from their ores, comprising a tank having an amalgamated copper lining forming a cathode and a multiplicity of agitators, each rotating on its own axis and at the same time traveling around the tank, the said agitators forming an anode and an electric circuit.

605835—June 21, 1898. E. and G. ANDREOLI. *Electrolytic production of amalgams, etc.*—An apparatus for the production of amalgam, consisting of a cell provided with positive and negative compartments separated by porous diaphragms, the negative compartments having a raised middle portion in the form of a table or block between the sides of which and the said partitions are narrow vertical spaces, the top of the block or table and the vertical spaces being covered and filled with a continuous body of mercury forming a cathode.

614572—November 22, 1898. J. C. McNULTY. *Method of and apparatus for treating ores.*—The art of extracting precious metals from their ores, consisting in mixing pulverized ore with an electrolytic fluid, causing the mixture to flow from one level to another between adjacent electrode plates of opposite polarity, passing an electric current between said plates and vibrating the electrodes in a direction substantially at right angles to the plane of said electrodes for the purpose of preventing the polarization thereof; and in apparatus for the electrolytic treatment of ores the combination of a plurality of vats arranged in pairs communicating at the top, adjacent electrode plates of opposite polarity suspended within said vats and connected with a source of electricity, vibratory supports for said electrodes, means for vibrating the same at substantially right angles to their planes, a pressure conduit for pulp leading to the bottom of the first vat to provide an upward current therethrough, and an exit at the bottom of the succeeding vat providing a discharge for the downward current of pulp overflowing from the top of the vat preceding.

616891—January 3, 1899. G. D. BURTON. *Electrolytic apparatus for treating metals and ores.*—In an electrolytic ore-treating apparatus, the combination of a tank for containing an electrolyte, an anode disposed in said tank, a cathode dis-

posed in said tank, a screen or deflector also disposed in said tank between the anode and cathode and adapted to distribute the ore or material being treated, said screen having a conductive surface connected to the negative pole of an electric source whereby it is adapted to collect a portion of the product reduced from the ore by the action of the current and the electrolyte.

617911—January 17, 1899. E. A. SMITH and M. H. LYNQ. *Method of extracting metallic ores.*—The wet process of extracting copper from its ores having precious metal therein, which consists in digesting the pulverized ore under action of heat and an oxidizing agent, in presence of sulphuric acid, exposing the dissolved sulphates to metallic copper for precipitation of the silver, treating the filtrate electrolytically to deposit the copper, evaporating the lean electrolyte to concentrate the free acid, and crystallize the metallic sulphates, and finally calcining such crystallized sulphates to properly regenerate them as oxidizing agents for reuse.

623322—April 25, 1899. L. PELATAN. *Apparatus for treating ores or the like.*—In apparatus, the combination with a circular vat, of a revolving anode, situated above and parallel to a mercury cathode, with an unobstructed space above the surface of the cathode, the said anode having arms which extend close to the peripheral wall of the vat and are suspended from a shaft, and are provided with pins or stirrers projecting upward and downward to within a short distance of the underlying cathode, and projections or baffles extending inwardly from the inner surface of the peripheral wall of the vat.

626972—June 13, 1899. T. CRANEY. *Electrolytic apparatus for deposition of metals from solution.*—In an electrolytic apparatus, the combination of an outer tank provided with suitable feed and discharge connections for the liquid into the bottom and top, respectively, and an electrolytic couple, composed of sheet or analogous electrodes each folded in a fabric, with oppositely projecting marginal portions and rolled together into a tight bundle and sealed in the tank, whereby the fabric inclosing the electrode forms a porous medium through which the electrode is compelled to flow.

627442—June 20, 1899. L. PELATAN. *Process of electrolytically treating ores.*—The improvement in processes of treating ores electrolytically, consisting in adding to a sludge, consisting of ore and water, a solvent and picric acid as an oxidizing agent and then passing an electric current therethrough.

631040—August 15, 1899. J. E. GREENAWALT. *Process of extracting precious metals from their ores.*—A process for the treatment of gold and silver ores which consists, first, in properly roasting the pulverized ore; second, placing the ore in a filtering-vat; third, washing the ore to remove soluble salts; fourth, in passing through the ore an electrolyzed solution consisting of a solution of chlorides—chiefly sodium and ferric chlorides—with a small percentage of bromides and small quantities of chlorine, bromine, and hypochlorous acid, with such other compounds as result from the electrolysis of a chloride and bromide solution; fifth, passing the solution after it leaves the ore through a precipitating-tank; sixth, passing the solution after it leaves the precipitating-tank through the positive or anode compartment of an electrolytic cell, keeping the solution separate and distinct from the solution in the negative or cathode compartment of the cell; and, seventh, returning the solution from the regenerating cell to the ore in the vat and passing it thence to the precipitating-tank, again to the regenerating cell, and again to the ore as often as may be required to effect the necessary saving of the values.

633544—September 19, 1899. H. S. BADGER. *Electrolytic apparatus for precipitating metals.*—A precipitating-tank comprising the tank body, having a mercury-coated surface in its bottom, a revoluble shaft suspended in the tank and provided with hollow arms having perforations on their lower sides to deliver air or vapor in proximity to the said surface, means for rotating the revoluble devices, means for introducing air or vapor to the hollow arms, and an electric circuit in which the shaft, agitating arms, and mercury-coated surface are located.

639766—December 26, 1899. L. E. PORTER. *Apparatus for extracting precious metals from ores.*—The combination of a rotatable barrel adapted to form the

cathode; a porous lining of non-conducting material arranged inside the barrel; a lining of filtering material arranged inside the non-conducting lining; anode plates arranged inside the filter lining; a source of electrical energy, having one pole connected with the barrel and the other pole connected with the anode plates.

640718—January 2, 1900. C. P. TATRO and G. DELIUS. *Process of extracting precious metals.*—In the process of separating precious metals from ores, the steps comprising electrolytically depositing a portion of the precious metals in the bath upon a drum cathode revolving partially immersed in the bath, at the same time scraping the said deposit from the drum, also simultaneously depositing other portions of similar precious metals in the same bath upon a cathode of sodium amalgam.

641571—January 16, 1900. W. WITTER. *Process of producing solution of cyanogen halide.*—The process for producing a solution of cyanogen halide by electrolyzing in a bath without a diaphragm and with inert electrodes a solution containing an alkali cyanide, an alkali halide, and the salt of a metal which forms an insoluble hydroxide.

649151—May 8, 1900. W. WRIGHT. *Apparatus for extracting metals from refractory ores.*—An apparatus for extracting metals from refractory ores, comprising a tank for receiving a sludge of such ores; a stationary, horizontal perforated partition in said tank, forming beneath it a chamber; a cathode on the bottom of the tank within said chamber; a filtering medium carried on the partition; a number of pins arranged in a series of concentric circles projecting upward from said partition; a main driving-shaft; a series of radial arms supported by said shaft, and a plurality of anodes carried by said arms and working between the series of concentric pins.

650646—May 29, 1900. F. H. LONG. *Apparatus for electrolytic reduction of ores.*—An electrolytic apparatus, the combination with a reducer vessel; its bottom cathode and a diaphragm above said cathode, of a set of dependent anodes, each consisting of a carbon head; a copper stem extended therefrom through the vessel; an incasing iron tube carried by the vessel head to sustain the anode pole; a vulcanite sheath for said tube, and suitable elastic gaskets to expansively close the joints.

653538—July 10, 1900. N. L. TURNER. *Electrolytic apparatus.*—An electrolytic apparatus, comprising a tank, rotary agitators located therein eccentrically, a series of electrodes whose main portion is concentric with the tank, while the portions adjacent to the agitators are curved concentrically with the axes of said agitators, and electrodes of opposite polarity to those first named.

654437—July 24, 1900. W. A. CALDECOTT. *Method of extracting gold from cyanide solutions containing the precious metals.*—Means for extracting gold from cyanide solutions in depositing cells, consisting in a mechanical mixture of zinc shavings and lead shavings.

656305—August 21, 1900. W. STRZODA. *Process of electrolytically extracting zinc from ores.*—The process of electrolytically extracting zinc from its ores, which consists in placing the disintegrated or pulverized ore in its natural state in an electrolytic vat containing an aqueous alkali-metal solution capable of dissolving the ore, with production of a zincate and in direct contact with the cathode, and closing the circuit through the vat, thereby precipitating zinc and the alkali metal at the cathode, the alkali metal reacting with the water to regenerate the solvent solution.

657032—August 28, 1900. A. M. ROUSE. *Apparatus for electrolyzing ores.*—In an apparatus of the class described having an anode and a cathode suitably arranged therein, the combination of a tank having an outer compartment, a tube located therein having an open upper end and provided at its lower end with openings forming communication from said compartment, a driving-shaft projecting within said tube, an inner cup carried by said shaft, wings carried by said cup, an outer cup carried by said wings, a discharge duct, and a valve arranged to close said duct.

662286—November 20, 1900. E. MORZ. *Electrolytic apparatus.*—In an electrolytic cell having open ends, the combination with a removable cross-bar and

means for supporting it in position, of a metallic plate covering the bottom and two sides of the bar, and forming the anode plate of the cell, of a metallic plate arranged horizontally below and parallel with the bottom of the cross-bar, so as to form a passage between such plate and the bottom of the cross-bar, such plate forming a cathode plate of the cell, and an auxiliary metallic cathode plate arranged vertically and parallel with the sides of the cross-bar and in circuit with the horizontal cathode plate, such vertically arranged plate extending below the plane of the bottom of the cross-bar, so as to more or less obstruct the said passage.

664537—December 25, 1900. J. DOUGLAS. *Process of extracting copper.*—The process of reducing copper ore and matte, which consists in electrolyzing solid cuprous chloride, employing the gases evolved in the treatment of copper ore and matte, employing the electrolyte resulting from the electrolyzing of the solid cuprous chloride as a solvent for the cuprous chloride so produced, and recovering the copper from the solution by electrolysis.

668812—February 26, 1901. A. M. ROUSE. *Apparatus for electrolytically extracting and depositing gold and silver from their ores.*—In an apparatus, the combination of a series of pulp-receiving tubs, anodes and cathodes arranged in said tubs, an agitation-tube having communication with said tubs at their upper and lower ends, an agitator arranged in said tube, perforated conduits located in the upper ends of said tubs, chutes located beneath said conduits onto which the ore pulp is discharged, and deflectors located beside said conduits adapted to direct the flow of pulp onto said chutes as it passes through said conduits.

669752—March 12, 1901. P. W. KNAUF. *Electrolytic apparatus.*—An element for an electrolytic series, consisting of a metallic receptacle having its lower portion of less diameter than the upper portion and having a bottom surface which is inclined upward radially from the center to the outer periphery, in combination with an exterior peripheral seat arranged below the upper edge, and an orifice adjacent to said seat.

669926—March 12, 1901. C. HOFFNER. *Process of electrolytical extraction of metals.*—A process which consists in placing a soluble metallic anode in a solution capable of dissolving the same, placing a suitable cathode in a second similar solution containing a metal more electropositive than that of the anode, interposing a third similar solution of less solution pressure between the two first mentioned, placing an auxiliary cathode therein, separating the solutions by suitable diaphragms, maintaining the solutions in motion and at a temperature above normal, passing a current, thereby dissolving the anode and precipitating the cathode metal at the cathode, and part of the diffused anode metal at the auxiliary cathode, precipitating the anode metal from the anode and intermediate solutions and returning the resulting solution when enriched in cathode metal to the cathode cell.

678526—July 16, 1901. C. P. STEWART. *Apparatus for the recovery of gold from cyanide solutions.*—An apparatus for recovering precious metals from flowing cyanide solutions, comprising in combination a relatively long substantially horizontal trough, means for supplying the solution at one end thereof, a partition near the receiving end of the trough for distributing the solution, a retaining partition at the discharge end of the trough adapted to retain the solution in the trough to the desired height, a body of quicksilver in the bottom of the trough between said partitions, a series of transverse anode supports extending substantially from partition to partition, a series of anodes adjustably mounted in said supports and extending down into the path of the flowing solution, and suitable electric connections.

682155—September 3, 1901. C. P. TATRO and G. DELIUS. *Electrolytic apparatus for extracting precious metals.*—In apparatus for extracting precious metals, a tub; a mercurial cathode in the bottom thereof, a principal anode, means for lowering it into and raising it out of the tub, and a minor anode permanently in the tub.

689018—December 17, 1901. W. ORR. *Method of recovering cyanides.*—The method of regenerating cyanide solutions which have become fouled by the presence of zinc and copper contained in the solutions, as double cyanide of zinc and

opper with the alkaline metals which consists, first, in passing through the solution from a series of zinc anodes to a corresponding series of metallic cathodes a current of electricity; next, in introducing into such solution alkaline hydrate, being hydrate of the monovalent alkali metals and hydrate of the divalent alkali metals in the proportion of about two to one; next introducing into the solution a soluble alkali-metal sulphide, and finally removing the resulting zinc-sulphide precipitate.

689674—December 24, 1901. A. I. IRWIN. *Machine for extracting metal from ores.*—In a machine for the automatic and continuous extraction and deposition of metal from ores at one and the same time, a treatment-tank, an endless anode traveling in said tank, the upper and lower stretches of the anode being in position to be immersed in the solution in the tank, diagonally disposed blocks of insulating material attached to said anode, cathodes in the tank, one under each stretch of the anode, and connections with a source of electricity.

689959—December 31, 1901. E. L. GRAHAM. *Process of disintegrating and comminuting minerals or ores.*—The process of treating ores, consisting of the following steps: First, immersing the ores in a solution of sulphuric and hydrofluoric acid; incapable of dissolving the ore; second, passing an electric current of sufficient strength to disintegrate the ore through the solution; and third, extracting the metal from the ore.

699964—May 13, 1902. F. H. LONG. *Electrolytic converter.*—In electrolytic converters, the combination with the closed reducer vessel having the anode and cathode terminals and the interposed diaphragm dividing the vessel into upper anode and lower cathode chambers, of a combined separator and vent-pipe connected to the cathode chamber beneath the diaphragm extending upwardly above the level of said diaphragm and having a free outlet for the gases.

700941—May 27, 1902. N. S. KEITH. *Process of treating copper or other ores for obtaining their contents of metals.*—The process of electrolyzing a solution of a metal; to deposit the metal therefrom, which consists in passing it as an electrolyte through a succession of two or more electrolytic cells, arranged so that the cells are connected in electrical series with a source of electricity; the anodes insoluble, the electrodes of each cell in electrical multiple, and having gradually increasing surfaces, whereby there is a gradual reduction of the current density as the metal of the electrolyte is deposited.

704639—July 15, 1902. C. HOFFNER. *Leaching and extraction of metals from their ores.*—The process of extracting metals, which consists in leaching a suitable material containing copper, lead, and silver, with a warm cupric-chloride solution containing a solvent of cuprous chloride, in quantity less than is required for saturation, thereby dissolving lead and silver chlorides, precipitating them, reconvertng the solution into cupric chloride, using the same for leaching fresh quantities of ore, leaching the residues with a similar hot solution more concentrated in cupric chloride, thereby dissolving copper and recovering those metals therefrom, reconvertng the resulting solution into cupric chloride, and returning the latter into the cycle of operations.

706436—August 5, 1902. F. T. MUMFORD. *Apparatus for the electrolytical treatment of ores or slimes.*—An apparatus for the extraction of metals from their ores and slimes, comprising a rotatable cylindrical metallic drum, a copper lining therein, a body of mercury in the drum to maintain the lining amalgamated, a valve-controlled inlet and outlet, and a relief-valve at one end, a plurality of conductive rods insulated from and passing longitudinally through the drum, a metallic ring connecting the bars, trailing electrical contact for the drum and one for said ring.

709817—September 23, 1902. C. E. DOLBEAR. *Electrolytically treating ores.*—The method of reducing metals from their ores, which consists in dissolving the crushed ore in a compound containing a nitric acid radical, adding to the mixture sulphuric acid, and subjecting the resultant compound to the action of an electric current.

725864—April 21, 1903. W. B. MCPHERSON. *Apparatus for the treatment of gold or other ores.*—A precipitating apparatus for depositing gold and silver from

a cyanide of potassium solution and from other chemical solutions, comprising a precipitating-box having downward, inclined bottom with openings therein, valves located in said openings, said box provided with a series of electric conducting plates vertically arranged therein and connected with a source of electric supply, a gauge receptacle, a pipe communicating with said receptacle and with the precipitating-box through which the said solution passes back and forth, a float within said receptacle and adapted to reciprocate therein, a yoke secured to said float, a horizontally reciprocating valve-rod, devices for connecting said yoke with said valve-rod, means for operating said valves in connection with valve-rod, and means for conveying said solution from said precipitating-box and returning the same thereto.

737554—August 25, 1903. I. P. BURROWS. *Electrolytic apparatus*.—An electrolytic apparatus, comprising a dissolving vessel having a revoluble anode, a depositing vessel having a cathode, means for conveying an unbroken stream of liquid from the dissolving vessel, and an electric circuit including said anode and cathode, whereby the electric current is caused to transverse the stream of liquid flowing from the dissolving vessel into the depositing vessel.

741231—October 13, 1903. W. H. DAVIS. *Process of treating cyanide solutions*.—The process for treating cyanide solutions during or subsequently to their contact with the ore, consisting in introducing into the solution an alkaline hydrate and then subjecting the mixture to the action of an alternating electric current, thereby raising the osmotic pressure to dissociate the double salts in the solution, causing precipitation of the hydrates of the base metals and to combine the freed cyanogen with the alkaline hydrates to cause simultaneous regeneration of the cyanide in the solution and clarifying of the latter.

741439—October 13, 1903. C. E. BAKER and A. W. BURWELL. *Process of treating ores*.—The process of recovering copper and nickel from a solution of sulphates of copper, nickel, and iron, which consists of electro-depositing the copper, neutralizing the solution, and electro-depositing the nickel with a current density insufficient to deposit the iron.

743668—November 10, 1903. R. SUCHY and H. SPECKETER. *Extracting chromium from chrome-iron ore*.—The process of making soluble chrome-iron ore and obtaining chromium compounds, which consists in heating the ore together with sulphuric acid in excess and an oxidizing agent and separating by filtration the precipitated insoluble ferrisulphate from the chromosulpho acid.

749843—January 19, 1904. H. R. CASSEL. *Process of extracting precious metals by electrolysis*.—The process of extracting precious metals by electrolysis, which consists in circulating the pulp between vertical electrodes, amalgamating a vertical cathode, successively deflecting the rebounding mercury back upon said cathode, removing the amalgam, neutralizing the alkali in the mercury, and returning the mercury to the cathode.

749844—January 19, 1904. H. R. CASSEL. *Apparatus for extracting precious metals by electrolysis*.—An apparatus for extracting precious metals by electrolysis, comprising a tank, inclosed vertical electrodes, mercury deflectors, and pulp-guards at the sides of the cathode, an elevated pulp-box, communicating perforated launders, means for lifting the pulp into said box, an elevated mercury pot, communicating slidable perforated troughs, and means for lifting the mercury into said pot.

755302—March 22, 1904. E. A. LE SUEUR. *Extraction of copper from comminuted mineral mixtures*.—The method of obtaining metallic copper from mixtures containing it, which consists, first in treating said mixtures with an ammoniacal solution containing a cupric compound or compounds, so as to dissolve the desired copper, then in removing a portion of the total copper contents of the solution, and lastly in using the partially exhausted solution over again to dissolve fresh copper as before.





## INDEX.

---

- Acetonitrile, 40  
 Adler's process, hydrocyanic acid, 93  
 Albright's process, sulphocyanide, 285  
 Alcoholic carbimides, 40  
 Allyl cyanide, 40  
 Aluminium cyanide, 24  
 Ammonium cyanate, 37  
     cyanide, 23  
     cyanhydrate, 60  
     sulphocyanate, 274  
     thiosulphocarbamate, 273  
 Ammoniacal liquors, 224  
     cyanogen from, 242  
     Prussian blue, 292  
 Amyl cyanide, 40  
 Andréoli's process, gold precipitation, 315  
 Antimony blue, 293  
 Apparatus, Bueb's, 186-8  
     Castner's, 142, 174  
     Engler's, 201  
     Mackey's, 136  
     Raschen's, 99  
     Stassfurter Chem. Fabrik, 159  
     Roca's, 167  
 Arnoul, Camille, works of, 248  
 Auriferous minerals, oxidation of, 295  
 Auripotassic cyanide, 35  
 Aurocyanide, 35  
 Aurosopotassic cyanide, 35  
 Azulmic acid, 11  
  
 Barium cyanide, 24, 169  
     ferricyanide, 32  
 Beck's process, ferricyanide, 266  
 Beilby's process, cyanide, 162  
 Bergmann's process, hydrocyanic acid, 94  
     cyanide, 101  
     results, 154  
 Beringer's process, cyanide, 150  
 Berthelot's hypothesis, 7  
 Black-mass, composition of, 204  
 Blackmore's process, cyanides, 150  
 Blood-lye, 81  
 Blue potash, 205  
  
 Bouxvillers Mines' process, ferricyanide, 264  
 Bower's process, cyanide, 107  
     ferricyanide, 243  
 British Cyanide Co.'s process, cyanide, 105  
     sulphocyanide, 283  
 Brock's process, sulphocyanide, 282  
 Brunquell's process, cyanide, 153  
     ferricyanide, 210  
 Bueb's apparatus, 186  
     process, cyanide, 185  
     ferricyanide, 237  
 Buignet's method, hydrocyanic acid, 48  
 Burchell's method, 52  
 Butyl cyanate, 40  
     cyanide, 40  
 Butyro nitrile, 40  
  
 Calcium cyanide, 24  
     ferricyanide, 32  
     sulphocyanate, preparation of, 277  
 Carbazol, 183  
 Carbylamines, 39  
 Castner's process, cyanide, 153  
 Cetyl cyanide, 40  
 Chaster's process, cyanide, 165  
     hydrocyanic acid, 88  
 Chem. Fabrik Aktiengesellschaft's process, cyanide, 165  
 Chlorides, detection of, 47  
 Chlorine process, ferricyanides, 261  
 Chromium cyanide, 25  
 Chryseane, 21  
 Clark's process, 16  
 Clauss and Domeier's process, ferrocyanide, 234  
 Coal, nitrogen content of, 220  
     types of, 216  
 Cobalt cyanide, 27  
     ferricyanide, 32  
 Cobalticyanide of potassium, 34  
     sodium, 34

- Cobaltocobalticyanide, 34  
 Coke, elements of, 218  
 Compagnie Générale des Cyanures, 273  
 Conroy's process, cyanide, 108  
     ferrocyanide, 211  
 Cooling-mixture, 329  
 Copper cyanide, 26  
     ferricyanide, 32  
 Crystallization, 210  
 Cyanamid, 147  
 Cyanate of ammonium, 37  
     silver, 37  
     sodium, 37  
 Cyanates, 44  
     detection of, 47  
     Hertig's method, 47  
 Cyanic acid, 36  
     esters, 40  
 Cyanide of aluminium, 24  
     ammonium, 23  
     barium, 24  
     calcium, 24  
     cobalt, 27  
     copper, 26  
     chromium, 25  
     gold, 27  
     iron, 25  
     manganese, 25  
     mercury, 26  
     nickel, 27  
     platinum, 27  
     silver, 26  
     sodium, 23  
     tin, 25  
     zinc, 24  
 Cyanides, analysis of commercial, 47  
     characteristics of, 328  
     critical temperatures, 324  
     density of, 323, 329  
     determination of medicinal,  
         48  
     double, 28  
     extraction from illuminating  
         gas, 214, 219  
     extraction from purifying ma-  
         terials, 245  
     extraction from sulphocya-  
         nides, 95  
     Fordos and Gélis' method, 45  
     heat of formation, 56, 324  
         solution, 324  
         volatilization, 324  
     O. Hertig's method, 47  
     Liebig's method, 44  
     list of works producing, 74  
     methods of manufacture, 81  
     simple, 22  
     solubility of, 327  
     strong solution, 301  
     use of, 294  
     weak solutions, 302  
 Cyanides—manufacturing processes\*  
     Adler's process, 93  
     Armengaud's process, 126  
     Beilby's process, 162  
     Bergmann's process, 94  
     Beringer's process, 101, 150  
     Blackmore's process, 150  
     Blairs' process, 126  
     Boussingault's process, 119  
     Bower's process, 107  
     British Cyanide Co.'s process, 105  
     Brunquell's process, 153  
     Bueb's process, 185  
     Bunsen's process, 123  
     Castner's process, 141, 153, 172  
     Chaster's process, 88, 165  
     Chem. Fabrik Aktiengesellschaft's,  
         183  
     Chem. Fabrik Pfersée Augsburg, 149  
     Chipmann's process, 138  
     Conroy's process, 107  
     Dalnot's process, 92  
     Deutsche Gold u. Silber Scheide  
         Anstalt, 175  
     Dickson's process, 129  
     Dzuik's process, 150  
     Etard's process, 110, 120  
     Finlay's process, 110  
     Fogarty's process, 128  
     Frank and Caro's process, 144, 153  
     Gen. Elec. Chem. Co.'s process, 152  
     Gilmour's process, 134  
     Glock's process, 179  
     Goerlich and Wichmann's process, 107  
     Grossmann's process, 182  
     Hetherington and Musspratt's pro-  
         cess, 106  
     Hood and Salamon's process, 169  
     Hornig's process, 170  
     Hornig and Schneider's process, 143  
     Hoyermann's process, 180  
     Huntington's process, 180  
     Karmrodt's process, 153  
     Kellner's process, 182  
     Kerp's process, 181  
     Lambilly's process, 129, 161, 178  
     Lance and Bourgade's process, 156  
     Liebig's process, 87, 153  
     Lucas' process, 153  
     Luttke's process, 104  
     Mackey's process, 135  
     Mactear's process, 157  
     Mallet's process, 121  
     Margueritte and Sourdeval's process,  
         126, 153  
     Martin's process, 179  
     Mehner's process, 137, 143  
     Moise and Mehner's process, 140  
     Mond's process, 127  
     Moulis and Sârs' process, 160  
     Newton's process, 126

**Cyanides—manufacturing processes:**

- Old processes, 85
- Ortlieb and Müller's process, 190
- Parkinson's process, 120
- Pestchow's process, 137
- Pictet's process, 121
- Pfleger's process, 165
- Playfair's process, 102
- Possoz and Boissière's process, 124
- Raschen and Brock's process, 97, 110
- Readmann's process, 135
- Roca's process, 166
- Rossler and Haaslacher's process, 89
- Roussin's process, 181
- Schneider's process, 171
- Silesia Verein Chem. Fabrik's process, 107
- Société Anonyme de Croix's process, 190
- Stassfurter Chem. Fabrick's process, 158
- Swan and Kendall's process, 137
- Synthetic processes, 111
- Tessié du Mothay's process, 120
- Vidal's process, 184
- Villepigne's process, 121
- Wagner's process, 88
- Weldon's process, 128
- Wichmann and Vautin's process, 88
- Wolfram's process, 150
- Young's process, 134
- Young and Macfarlane's process, 163

**Cyaniding mixture, 168**

- Cyanogen, constitution of, 5**
  - conversion tension, 14
  - formation, 12
  - preparation, 13
  - properties, 10

**Cyanosulphite of potassium, 22**

- Dalinot's process, hydrocyanic acid, 92
- Deiss and Monnier's process, sulphocyanide, 281
- Deutsche Gold u. Silber Scheide Anstalt's process, ferrocyanide, 265
- DeWilde's process, 303
- Donath's process, ferrocyanide, 258
- Donath and Margosche's method, ferrocyanide, 53
- Double cyanides, 28
- Dubosc's process, ferricyanide, 265
- du Castelet Works' process, ferrocyanide, 213
- Dzuik's process, cyanide, 150

- Engler's apparatus, 201
- Erlenmeyer's method, ferrocyanide, 49
- Esop's process, ferrocyanide, 258
- Etard's process, hydrocyanic acid, 94
- Ethyl cyanate, 40
  - cyanide, 40

**Everitt's process, 16**

- Feld's process, ferrocyanide, 241
- Ferricyanide, manufacture of, 261
  - of potassium, 43, 32

**Ferricyanide processes:**

- Beck's process, 267
- Chlorine process, 261
- Deutsche Gold u. Silber Scheide Anstalt's process, 265
- Dubosc's process, 265
- Kassner's process, 266
- Mines at Bouxvillers, 264
- Reichardt's process, 263
- Williamson's process, 267

**Ferricyanide, use of, 319**

- Ferrocyanide, 25, 43**
  - manufacture of, 192, 205, 229

**Ferrocyanide processes:**

- Bower's process, 243
- Brunquell's process, 210
- Bueb's process, 237
- Clauss and Dumeier's process, 234
- Conroy's process, 212
- Donath's process, 258
- Esop's process, 258
- Feld's process, 241
- Fowles' process, 233
- Gasch's process, 232
- Gauthier-Bouchard's process, 248
- Goerlich and Wichmann's process, 213
- Harcourt's process, 257
- Hempel's process, 257
- Hetherington's process, 212
- Holbling's process, 259
- Karmrodt's process, 211
- Knublauch's process, 231
- Kunheim's process, 257
- Lewis' process, 236, 243, 250
- Marasse's process, 258
- Maslow's process, 259
- Musspratt's process, 212
- Pendrie's process, 242
- Richter's process, 258
- Rowland's process, 233
- Schroeder's process, 234
- Teichmann's process, 235
- Valentin's process, 256
- Wolfram's process, 257
- Works du Castelet, 213
- Ferrocyanide, detection of:**
  - Burchell's method, 52
  - Erlenmeyer's method, 49
  - Knublauch's method, 50
  - Moldenhauer and Leybold's method, 51
- Ferrocyanide of iron, 31**
  - potassium, 29
  - sodium, 31
- Ferrocyanide, precipitation of, 253**
  - use of, 316

- Filtering-vats, 300  
 Flemming's furnace, 158  
 Fordos and Gélis' method, 45  
 Formates, detection of, 47  
 Frank and Caro's process, cyanide, 144  
 Furnaces, Flemming's, 158  
     Gruneberg's, 158  
     reverberatory, 199  
     Siepermann's, 158, 182
- Gas, composition of, 226  
 Gasch's process, ferrocyanide, 232  
 Gauthier-Bouchard's process, ferrocyanide, 248  
 Gélis' process, sulphocyanide, 272  
 Gen. Elec.-Chem. Co.'s process, cyanide, 182  
 Goerlich and Wichmann's process, cyanide, 107  
 Goerlich and Wichmann's process, ferrocyanide, 213  
 Goerlich and Wichmann's process, sulphocyanide, 286  
 Gold-bromine cyanide, formation, 297  
 Gold cyanide, 35  
     precipitation of, 298, 304, 314  
     solution of, 298  
 Grossmann's process, cyanide, 182  
 Gruneberg's furnace, 158
- Harcourt's process, ferrocyanide, 257  
 Hempel's process, ferrocyanide, 257  
 Hertig's method, cyanates, 47  
 Hetherington's process, ferrocyanide, 212  
 Hetherington and Muspratt's process, cyanide, 106  
 Holbling's process, ferrocyanide, 259  
 Hood and Salamon's process, cyanide, 169  
     sulphocyanide, 282
- Hornig's process, cyanide, 170  
 Hornig and Schneider's process, cyanide, 143  
 Hydrate of iron, composition, 247  
 Hydrocyanic acid, 14, 42  
     Buignet's method, 48  
     heat of formation, 57
- Hydrocyanic acid:  
     Adler's process, 93  
     Bergmann's process, 94  
     Chaster's process, 88  
     Dalinot's process, 92  
     Etard's process, 94  
     Liebig's process, 87  
     Rossler and Haaslacher's process, 89  
     Wagner's process, 88  
     Wichmann's and Vautin's process, 90
- Illuminating-gas, composition, 226  
     elements of, 218
- Karmrodt's process, cyanide, 153  
     ferrocyanide, 211  
 Kassner's process, ferricyanide, 266  
 Keith's process, gold precipitation, 314  
 Kellner's process, cyanide, 182  
 Kerp's process, cyanide, 181  
 Knublauch's process, ferrocyanide, 231  
 Kunheim's process ferrocyanide, 257
- Lambilly's process, cyanide, 153, 161  
 Laming mixture, composition, 246  
 Lance and Bourgade's process, cyanide, 156  
 Lewis' process, ferrocyanide, 236, 243, 259  
 Liebig's method, cyanide, 44  
     process, cyanide, 153  
     hydrocyanic acid, 87  
     theory, 9
- Limonite, composition of, 247  
 Lixiviation, 210, 249  
     vats, 252
- Lucas' process, cyanide, 153  
 Luttke's process, cyanide, 104  
 Lux mass, composition, 246
- MacArthur and Forrest's method, 304  
 Mackey's process, cyanide, 135  
 Mactear's process, cyanide, 157  
 Manganese cyanides, 25, 34  
 Marasse's process, ferrocyanide, 258  
 Margueritte's process, cyanide, 153  
 Margueritte and Sourdeval's process, cyanide, 126
- Martin's process, cyanide, 179  
 Maschow's process, ferrocyanide, 258  
 Mehner's process, cyanide, 143  
 Melam, 39  
 Mercury cyanide, 26  
 Metal, production of, 197  
 Metallic cyanides, 18  
 Methyl cyanate, 46  
     cyanide, 40
- Moise and Mehner's process, cyanides, 140  
 Moldenhauer and Leybold's method, 51  
 Mond's process, cyanide, 127  
 Monthier's blue, 292  
 Moulis and Sârs' process, cyanide, 160  
 Mulholland's process, 303  
 Muspratt's process, ferrocyanide, 212
- Newton's process, cyanide, 126  
 Nickel cyanide, 27  
     ferricyanide, 32
- Nitriles, 39  
 Nitroferri-cyanides, 35  
 Nitroprussiates, 35  
 Non-synthetic processes, 85
- Old process, cyanide, 85  
     ferrocyanide, 193
- Organic compounds, 39  
 Ortlieb & Müller's process, cyanide, 190

Oxide of iron, composition of, 247  
Oxygen compounds of cyanogen, 36

Paracyanogen, 13, 147  
Pendrie's process, ferrocyanide, 242  
Pfleger's process, cyanide, 165  
Physical study cyanogen, 10  
Platinum cyanide, 27  
Platino cyanides, 34  
Playfair's process, cyanide, 102  
Potash, determination of, 48  
Potassium cyanate, 36, 60  
    cyanide, 20, 58  
        analysis of, 47  
        antidote, 22  
        heat of formation, 58  
        manufacture, 85  
        production, 72  
        use of, 70  
    cyaniferide, 32  
    cyanosulphite, 21  
    ferricyanide, 32  
        production, 72  
    ferrocyanide, 29, 43, 49  
        exportation, 80  
        heat of formation, 60  
        importation, 79  
        production, 72  
    sulphide, detection, 47  
    sulphocyanide, 38  
Processes utilizing ammonia, 153  
    atmospheric nitrogen, 117  
Propionitrile, 40  
Propyl cyanide, 40  
Prussian blue, 31  
    determination, 54  
    discovery of, 69  
    manufacture, 288  
    use of, 319  
    Woodward's method, 289  
Prussic acid, 14  
    action on system, 17  
    antidote, 18  
Purifying materials, 50  
    composition, of, 219,  
    226, 245  
    revivification, 247

Raschen's apparatus, 99  
Raschen and Brock's method, 97  
Raschen, Davidson and Brock's process, cyanide, 110  
Readmann's process, cyanide, 135  
Red prussiate of potash, 32  
Reichardt's process, ferricyanides, 263  
Retort, 198  
Rhodanides, 37  
Richter's process, ferrocyanides, 258  
Roca's apparatus, 167

Roca's process, cyanide, 166  
Rossler and Haaslacher's process, hydrocyanic acid, 89  
Roussin's process, cyanides, 181  
Rowland's process, ferrocyanide, 233  
Schneider's process, cyanide, 171  
Schroeder's process, ferrocyanide, 234  
Siemens and Halske's process, gold precipitation, 314  
Siepermann's furnace, 158, 182  
Silesia Verein Chem. Fabrik's process, cyanide, 107  
Silver cyanate, 37  
    cyanide, 26  
    ferricyanide, 32  
Simple cyanide, formation, 19  
    properties, 19  
Société Anonyme de Croix's process, cyanide, 190  
Sodium cyanate, 37  
    cyanide, 23  
    ferrocyanide, 31  
Soluble Prussian blue, 32, 292  
Sourdeval's process, cyanide, 153  
Spent oxide, 54  
    composition, 246  
Stassfurter Chem. Fabrik's process, cyanide, 158  
Sulman's process, 303  
Sulphate of iron, composition of, 247  
Sulphocarbamide, 39  
Sulphocyanates, 37  
Sulphocyanide, 37, 43, 50  
    cost of, 271  
    detection of, 47  
    manufacture, 269  
Sulphocyanide processes:  
    Albright's process, 285  
    British Cyanide Co.'s process, 283  
    Brock's process, 282  
    Deiss and Monnier's process, 281  
    Gélis' process, 270  
    Goerlich and Wichmann's process, 286  
    Hood and Salamon's process, 282  
    Tcherniac's process, 285  
Sulphocyanide recovery, 56  
    use of, 319  
Swan and Kendall's process, cyanide, 137  
Synthetic processes, cyanide, 111  
Tables, 294  
Tar, 218  
Tcherniac's process, sulphocyanide, 285  
Teichmann's process, ferrocyanide, 235  
Tin cyanide, 25  
Thomson's process, 16  
Toxicological research, 54  
Tricyanates, 37  
Turnbull's blue, 33, 292  
Valentin's process, ferrocyanide, 256

- Vats, filtering, 299  
Vauquelin's process, 16  
Vidal's process, cyanide, 184  
  
Wagner's process, cyanide, 88  
Weldon's process, cyanide, 127  
Wichmann and Vautin's process, cyanide, 90  
Williamson's process, ferricyanide, 267  
Wolfram's process, cyanide, 150  
  
Wolfram's process, ferrocyanide, 257  
Woodward's method, 289  
  
Young's process, cyanide, 134  
Young and Macfarlane's process, cyanide, 163  
  
Zaloziecki's method, ferrocyanide, 52  
Zinc cyanide, 24  
    potassium cyanide, 22

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